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ON THE COLOR CHANGES OCCURRING IN THE BLUE FLOWERS OF THE WILD CHICORY, CICHORIUM INTYBUS

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Two varieties of the wild chicory, *Cichorium intybus*, are abundantly distributed over certain parts of Virginia and the District of Columbia, a more common blue variety and a rarer albino variety having white flowers. Several years ago the attention of one of us (Kastle) was called to the fact that the blue flowers of the wild chicory turned white and then brown, these changes occurring with great rapidity. The blue chicory occurs very abundantly in the immediate vicinity of the University of Virginia, so that an excellent opportunity presented itself for a closer inquiry into the cause of these interesting color changes exhibited by this blue flower.

A closer study of this phenomenon has revealed the following facts: The flowers of the blue chicory open in the morning, usually between seven and eight o'clock. When perfectly fresh the flowers have a light blue color and occasionally show a lavender or pinkish coat. Thus the flowers gathered by Mr. Haden on the morning of July 19 were distinctly pink near the base of the corolla. Even when left undisturbed upon the plant these blue flowers soon begin to

bleach and gradually lose their blue color, this change usually beginning at the outermost tips of the petals (corolla) and gradually extending in to the point at which the corolla is attached to the stem. The blue color nearly always persists in the stamens and pistil long after it has disappeared from the corolla. The composite flower gradually closes during the day and turns brown, so that after several days it is reduced to a nodule of brown, dry vegetable material. The rapidity with which these changes take place in the undisturbed flower seems to depend very largely on atmospheric conditions. On hot, moist days the flowers have frequently bleached and closed and have turned brown before noon. In other instances and under other atmospheric conditions they may retain their blue color until two or three o'clock in the afternoon, but always before the close of the day on which they bloomed; these blue flowers first turn white and close and are converted into a brownish mass of vegetable matter. When the flowers are pulled they pass through precisely the same changes of color and the same phenomena are observed as occur in those flowers which have been left undisturbed upon the plant. We shall show in this communication that these changes can be brought about even *in vitro*. It frequently happens that in bleaching the blue flowers become distinctly pink.

In the blue chicory, then, we have a flower which in the course of a few hours shows a most striking succession of color changes, namely, from blue to pink, or from blue to white, and then brown. As a matter of fact, this phenomenon is so striking that it has to be seen in order to be fully appreciated. It is well known, of course, that a great variety of flowers gradually alter in color as they fade and ultimately become brown. There are very few, however, which show a distinct succession of color changes during their life cycle, and so far as we are aware there are none, other than the blue chicory, in which these color changes are complete in a few hours.

Like other varieties of anthocyanin, the blue pigment of these flowers becomes bright carmine-red or rose-red on the addition of hydrochloric acid and yellowish green on the addition of alkali. We have made use of this reaction in follow-

ing the color changes occurring in this flower. In our efforts to arrive at the cause of the color changes occurring in the blue chicory we have studied the conduct of the flowers in light and darkness and also in chloroform vapor and in hydrogen. Secondly, we have studied the conduct of the flower pigment towards acids and alkalis and also towards the oxidases, peroxidases and various oxidizing agents. Lastly, we have observed that the flowers of both the blue and white chicory contain a powerful oxidase which in our opinion is responsible for the destruction of the flower pigment and the turning brown of the flower. The results of these observations are given in the following.

In the first place, it should be observed, in passing, that like all biochemical processes these color changes in the flower are dependent on a certain degree of moisture. With reasonable care these blue flowers can be pressed and dried between the folds of bibulous paper without losing their blue color. When perfectly dry they retain their blue color for months, indicating that water is essential to the bleaching. It has also been observed that the flowers of the blue chicory turn white somewhat more rapidly in the dark than in the light, so that exposure to sunlight cannot be the cause of this phenomenon.

Among other things, it occurred to us to test the behavior of the freshly gathered blue flowers in chloroform vapor. A stem of the freshly gathered plant, bearing a number of fully bloomed blue flowers, was placed in a small beaker of water and the whole placed in a tall desiccator containing some absorbent cotton saturated with chloroform. The first effect of the chloroform was to cause the flower to open out straight and full like a daisy. The blue petals began to show signs of bleaching almost immediately, and in twelve minutes after placing in the chloroform vapor the petals were nearly white. In twenty minutes the blue color had disappeared from the petals completely and only the stamens and pistil were blue. In twenty-five minutes the petals presented a shriveled appearance and were translucent and waxy looking. In forty-five minutes they were light brown in color and much

shriveled, and after one hour and ten minutes no trace of blue color was visible anywhere in the flower except in the stamens and pistil.

A second test of the effect of chloroform vapor on the blue flowers gave the following results. Some of the flowers were put in the chloroform vapor at 8.32 A. M. The petals of many of these flowers began to shrivel almost immediately and to turn pink. Some few, however, retained their original form and bleached quickly as described in the foregoing paragraph. In nine minutes many of the flowers had bleached and after thirteen minutes exposure they were removed from the chloroform vapor and the petals macerated with a small amount of 0.1 N hydrochloric acid. These gave only a faint pink color with the acid, indicating that only a little of the flower pigment remained, about as much, in fact, as remained in the petals of the flower which had bleached and faded normally in the air. In this connection it is to be noted that the fresh blue flowers give a deep carmine-red solution on maceration with 0.1 N hydrochloric acid. By way of comparison with the foregoing experiments in chloroform vapor, another stem bearing fresh blue flowers was placed in water and put in a desiccator without chloroform. After twelve minutes the flowers were unchanged and blue. At the end of forty-five minutes they were still blue. In one hour and fifteen minutes they had begun to turn white, this change first showing itself on the outermost tips of the corollas. After three hours, however, there was still some blue color to be observed near the central portions of the corollas. It was also observed that in passing to white these blue flowers tended to become pink. It is evident, therefore, that these color changes in the blue chicory are greatly accelerated by chloroform. This is not difficult to understand when it is borne in mind that these color changes are in some way associated with the gradual death of the flower. Hence, anything like chloroform which would tend to poison the flower ought to hasten these color changes.

We have also studied the conduct of the blue flower in hydrogen. A stem of the plant bearing blue flowers was

placed in a small beaker of water and the whole set under a bell jar through which a current of hydrogen was passing. After forty minutes the flowers were observed to have a slight pink color. At the end of an hour and ten minutes they appeared slightly shriveled and somewhat more pink. After one hour and forty minutes the flowers were still blue, but showed also a pink tint. At the end of six and a half hours the petals were found to be considerably shriveled, translucent and waxy in appearance, and almost entirely pink. The stamens and pistil were plum colored and very little, if any, of the blue color was left. A number of the petals, which were sticky to the feel, were macerated with 1 cc. 0.1 N hydrochloric acid and water. A rose-red solution was thus obtained, showing the presence of considerable amounts of the flower pigment.

On the other hand, the blue flowers which had been left exposed to the air during this interval, to serve as a control on the hydrogen experiment, had long since bleached, withered and turned brown. The petals of these flowers were found to contain only traces of the flower pigment. In a second observation some of the freshly gathered flowers were placed in hydrogen at 8.30 A. M. on July 21, and an equal number of flowers were left exposed to the air by way of comparison. After half an hour the flowers in hydrogen had become decidedly pink and a few of the petals showed slight evidences of bleaching at the tip. All of the flowers which had been left exposed to the air had bleached greatly, the color otherwise remaining being blue. All of them had withered somewhat, and one was closed entirely. One flower also was entirely white. At the end of an hour the flowers in hydrogen had shown no further change except that they had become somewhat more pink in color. The flowers which had been kept in the air were all withered by this time and all of them had become almost white, the only blue color remaining being in the stamens and pistil and at the point of attachment of the corolla to the stem. At 10 A. M. the flowers in hydrogen were all open except one and all were pink, although some blue color remained, giving a sort of lavender tint. In the air all

of the flowers were closed except one and all were white. The contrast in color and general appearance between these two lots of flowers at this time was very striking. The flowers in hydrogen stood until 10 A. M., July 23rd. At this time three of the flowers were found to be open, somewhat shriveled and deep pink in color. Three of the flowers had bleached and one was closed. The bleached flowers gave only traces of pink on maceration with 0.1 N hydrochloric acid, whereas the pink flowers gave a rose-red solution, indicating the presence of considerable amounts of flower pigment. The flowers which had been kept in the air during this time had changed to small, dark brown masses. It is clear, therefore, that hydrogen greatly retards those processes resulting in the destruction of the flower pigment in the flowers of the wild chicory. In this respect it exercises a protective and conservative action on the coloring matter contained in these flowers. As a matter of fact, the conduct of the flower in hydrogen, as compared with air, naturally suggests that in some way oxygen is concerned in these changes. It was thought at one time that the bleaching observed in this flower was due to a migration of the coloring matter from the corolla to the stamens and pistil. It is certain that these parts of the flower remain blue long after the corolla has become perfectly white. In order to test this point, a quantity of the fresh blue petals were cut off near the base of the flower. These were used as follows:

(1) Some of the fresh blue petals were placed in chloroform vapor. They bleached very rapidly, becoming pink during the process.

(2) Some of the fresh blue petals were pressed and dried between the folds of fine filter paper. These retained their blue color and have kept their color unchanged for over a month.

(3) Some of the cut petals were allowed to remain in the air, in the light. These gradually bleached, much less rapidly, however, than those in chloroform vapor.

(4) Some of the cut petals were allowed to remain in the air, in the dark. These also bleached at about the same rate as those in the air, in the light.

In none of these experiments was there any evidence of any migration of the flower pigment from one part of the corolla to the other. It is clear, therefore, that the bleaching of the blue chicory is not due to a migration of the coloring matter from the corolla to the stamens and pistil, but rather to some chemical change within the tissues of the corolla itself. Reference has already been made to the fact that the flower pigment turns bright carmine-red on the addition of a small amount of 0.1 N hydrochloric acid. We have also pointed out that the blue flowers of the chicory tend to turn pink under certain conditions. It therefore occurred to us that possibly changes in the reaction of the cell contents in the pigment cells might be responsible for the changes of color observed in the blue flower. With a view to testing this point a quantity of the blue petals were macerated in a porcelain mortar with 1 cc. 0.1 N hydrochloric acid. To the red mass 10 cc. of water was added and the mixture filtered. A clear carmine-red solution was thus obtained which has been found to keep unaltered for a number of days. To some of this red solution 0.1 N sodium hydroxide was gradually added. After a certain amount had been added a beautiful blue solution was obtained, exactly matching in tint the color of the fresh blue flower. On the addition of still further amounts of 0.1 N sodium hydroxide the solution gradually became lighter in color, until finally a perfectly colorless solution was obtained, corresponding, of course, to the colorless condition of the flower after it has bleached. On the addition of still more 0.1 N sodium hydroxide the colorless solution became bright yellowish green. If now more hydrochloric acid is added the solution again becomes carmine-red and on this solution the succession of colors with alkali could be again obtained. The red, blue and colorless solutions of the flower pigment have all been found to be acid to phenolphthalein and even the yellowish-green solutions do not always give an alkali reaction with this indicator. In other words, it would seem that in the variety of anthocyanin contained in the flower of the blue chicory we have an indicator capable of indicating various amounts of acid. It is also clear that the

particular color displayed by the flower of the blue chicory, whether pink, blue or white, will depend on the acidity of the cell contents of the pigment cells. If they contain relatively large amounts of acid the flower will be pink; if smaller amounts, it will be blue; and if still smaller amounts, white. As a matter of fact, it not infrequently happens that certain corollas of this flower show all three colors simultaneously, distributed over different areas of the corolla. In this connection it is interesting to note that the buds of the blue weed, *Echium boreale, L.*, are pink in color, whereas the corolla of the full-blown flower is blue. In all likelihood this pronounced difference in color is due merely to a difference in acidity.

On the other hand, it has been observed that the bleached petals of the blue chicory, especially after they have begun to shrivel and turn brown, contain very little of the flower pigment. On maceration with 0.1 N hydrochloric acid such petals give only traces of pink. It would seem, therefore, that another agent whose action has resulted in the complete destruction of the flower pigment has been at work in the bleaching and browning of these blue flowers. That such is the case is indicated by the following:

We have already seen that the conduct of the blue flowers in hydrogen is such as to indicate that the bleaching of the flower and the destruction of the flower pigment are due to oxidation. In this connection it is interesting to note that on maceration with water the blue flowers yield a red solution. This color is soon lost, however, and the solution turns brown. Such aqueous extracts of the blue flower give the guaiacum reaction directly, indicating the presence of an oxidase.

The rapid oxidation of the flower pigment by an oxidase would also explain the results which we have obtained with acetic and malic acid. When the blue flowers are macerated with 1 cc. 0.1 N acetic or malic acid and the macerated mass diluted with water, rose-red solutions are obtained, but by the time these are filtered it is found that the filtrates have lost their rose-red color and show only traces of anthocyanin on the addition of dilute hydrochloric acid. In this connection it has been found that extracts of the blue flower with

these weak acids blue guaiacum, whereas extracts of the flower in 0.1 N hydrochloric acid, in which the flower pigment is stable, do not give the guaiacum reaction. In other words, the oxidase has been destroyed by the stronger acid and hence the flower pigment escapes oxidation. The weaker acids, however, do not destroy the oxidase and hence in such extracts, as also in water, the flower pigment is destroyed by oxidation. In the light of these results it is only logical to ascribe the destruction of the flower pigment in this blue flower to the action of an oxidase. That such is the case has been proven in the following manner:

A number of the blue petals were macerated with 1 cc. 0.1 N hydrochloric acid and a small quantity of distilled water added. The bright rose-red solution was then filtered and 0.1 N sodium hydroxide added until the solution became bluish green in color. Three tubes were then prepared, each containing 3 cc. of this solution. These were labeled (1), (2) and (3), respectively. To (1) 1 cc. of distilled water was added, to (2) 1 cc. of a boiled aqueous extract of the blue flower, and to (3) 1 cc. of an active (unboiled) aqueous extract of the blue flower. The three tubes were then allowed to stand fifteen minutes at ordinary temperature. At the end of this time 1 cc. of 0.1 N hydrochloric acid was added to each tube, with the following results:

(1) became rose-red in color;

(2) became rose-red in color;

(3) remained yellowish brown and showed no pink color at all.

This proves conclusively that the flower pigment of this blue flower is destroyed by an aqueous extract of the flower itself.

If now the destruction of the flower pigment is due to an oxidase contained in the flower, then it is more than likely that the coloring matter of the flower would be destroyed by plant oxidases from other sources, and in fact by all of those oxidizing agents which blue guaiacum directly. In order to test this point the following experiment was carried out. A number of the blue petals were macerated in a porce-

lain mortar with 1 cc. 0.1 N hydrochloric acid, in order to extract the flower pigment and at the same time to destroy the oxidase of the flower. About 10 cc. of water was added to the macerated mass and the mixture filtered. Then 0.1 N sodium hydroxide was added gradually to the rose-red filtrate until the solution became colorless or faintly blue. Three tubes were then prepared, each containing 3 cc. of this solution of the flower pigment. These were labeled (1), (2) and (3), respectively. To tube (1) there was added 1 cc. of water; to (2) 1 cc. of a boiled, aqueous extract of the peel of the potato; to (3) 1 cc. of an active (unboiled) aqueous extract of the potato peel. These tubes were then allowed to stand at ordinary temperature for fifteen minutes, at the end of which time 1 cc. of 0.1 N hydrochloric acid was added to each, with the following results:

(1) became rose-red;

(2) became rose-red;

(3) remained yellowish brown and failed to show any trace of pink color.

This experiment goes to show conclusively that the flower pigment of the blue chicory is oxidized by the oxidase of the potato.

The colorless solution of the flower pigment is also readily oxidized and destroyed by the following substances: potassium ferricyanide, potassium permanganate, quinone, dilute solution of iodine, and by a 0.3 per cent. solution of hydrogen peroxide under the influence of various catalysts, such as platinum black, manganese dioxide and lead peroxide. As is well known, all of these substances blue guaiacum directly. It is more than likely, therefore, that any substance or mixture which gives the guaiacum reaction will oxidize and destroy the flower pigment of the blue chicory.

In this connection it is interesting to note that the flowers of the white chicory also contain a powerful oxidase. The white flowers contain no anthocyanin, however, and hence do not exhibit the color changes shown by the blue variety. They wither rapidly, however, and turn brown as is the case

with the blue variety, and in these changes the oxidase is undoubtedly concerned.

SUMMARY

The flowers of the blue chicory fade and wither with great rapidity. In so doing they exhibit certain marked changes of color, changing from blue to pink, from blue or pink to white and finally to brown, with practically complete destruction of the flower pigment.

It has been conclusively shown that these changes of color are due in part to variations in the amount of acid contained in the pigment cells and in part to the action of an oxidase[1] contained in the flower which completely oxidizes and destroys the flower pigment.

It has also been shown that other plant oxidases and various other oxidizing agents can affect the oxidation of the flower pigment into nonchromogenic products.

UNIVERSITY OF VIRGINIA
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[Contribution from the Kent Chemical Laboratory of the University of Chicago]

STEREOISOMERIC CHLORIMIDO KETONES[2]

BY PETER P. PETERSON

In 1903 Stieglitz and Earle,[3] in the course of their work on the theory of the "Beckmann Rearrangement," discovered the first representatives of a new group of stereoisomeric

[1] The word oxidase is here used in its usual signification, viz., as being an unstable, biologically active substance capable of oxidizing guaiacum, aloin and phenolphthalin, etc., directly. Quite recently Miss Wheldale (P. Roy. Soc., B, **84**, 121–124) has advanced the view that the browning of many plant extracts is due to the oxidation of pyrocatechinol under the influence of air and a peroxidase, and that the plant oxidase is in reality a mixture of pyrocatechinol, or the product of its autoxidation, and a peroxidase; in other words, that the power of plant extracts to blue guaiacum is due to an oxidation accomplished by the autoxidation product of pyrocatechinol under the activating influence of a peroxidase. It is scarcely necessary to add that this hypothesis regarding the nature of the plant oxidase in no way affects our view regarding the destruction of the anthocyanin in the bleaching of the flowers of the blue chicory. Our findings are that the anthocyanin in this flower is destroyed during its bleaching by an oxidase which is present or developed within the flower itself. This, of course, postulates nothing regarding the nature of the oxidase.

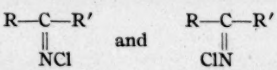
[2] See a preliminary paper by J. Stieglitz and P. Peterson: Ber. d. chem. Ges., **43**, 782 (1910).

[3] THIS JOURNAL, **30**, 399 (1903).

nitrogen derivatives, in which the stereoisomerism depends on the "syn" and "anti" positions of a chlorimide group in chlorimido esters:

Later Stieglitz and Hale[1] obtained a second pair of such stereoisomeric chlorimido esters and showed under what conditions the labile form can be converted into the stable variety. Finally Hilpert,[2] by preparing five other pairs of stereoisomers and determining the conditions for the transformation of the members of a pair reversibly into each other, established their existence on a sufficiently broad basis. These isomers are interesting, partly because of the simple character of the radical (Cl^+) attached to the nitrogen atom, and partly because of the light they shed on the question of the "Beckmann Rearrangement."[3]

The stereoisomers heretofore prepared, have in all cases been chlorimido esters. They made probable the existence of stereoisomerism also for chlorimido ketones,



comparable with the stereoisomeric ketoximes and hydrazones of Hantzsch and Werner and of the former's collaborators. The isolation of such stereoisomers seemed desirable, not only as confirming the conclusions reached in the work on the chlorimido esters, but also because it was thought their preparation would settle, experimentally, important questions connected with the "Beckmann Rearrangement." In the rearrangement of ketoximes, R—C(:NOH)R′, under the influence of phosphorus pentachloride, many chemists are inclined to assume[4] the formation of such chlorimides, R—C(:NCl)—R′,

[1] Unpublished results.

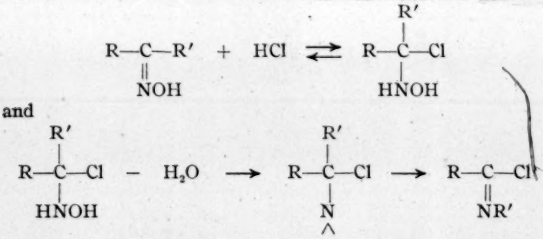
[2] This Journal, **40**, 155 (1908).

[3] See a later paper, to be published by Stieglitz, covering unpublished results with Hale and Eckstein.

[4] Cf. Hantzsch: Ber. d. chem. Ges., **35**, 3579 (1902).

as intermediate products, the first products isolated in the reaction being arylimidoacyl chlorides. These are supposed to be formed according to the scheme

According to the theory advanced by Stieglitz, such chlorimides would not be intermediate products; the rearrangement is supposed to be due to the anhydrizing power of phosphorus pentachloride and the other reagents used to accomplish the rearrangement, an intermediate product, containing *univalent* nitrogen, being considered to be the actual substance undergoing the rearrangement. For instance, we would have:[1]



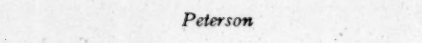
At the suggestion and under the direction of Professor Stieglitz, I undertook the problem of isolating, if possible, such

[1] In confirmation of these views, Stieglitz and Reddick have recently found that triphenylmethylhydroxylamine, $(C_6H_5)_3C.NHOH$, whose structure corresponds to that of the assumed intermediate addition product with hydrogen chloride, undergoes the "Beckmann rearrangement" with remarkable ease and smoothness under the influence of a dehydrating agent (phosphorus pentachloride was used). This result is the more noteworthy as it forms a striking contrast to the fact that hitherto all attempts to effect a rearrangement of chlorimidobenzophenone, $(C_6H_5)_2C : NCl$, have been unsuccessful (Stieglitz and Watkins). G. Schroeter has recently (Ber. d. chem. Ges., **44**, 1201 (1911)) brought valuable experimental evidence supporting the above theory. Experiments have been undertaken in this laboratory toward establishing a connection between the rearrangement and the *electrical charges* on the atoms involved. It is thought that, in the final instance, the significance of the rôle of the univalent nitrogen atom will be found to lie in such electrical relations. In a later paper these views will be discussed more elaborately and due consideration given to the confirmative experimental work of Schroeter, as well as to the criticisms of J. Stieglitz, Montagne (*Ibid.*, **43**, 2014 (1910)) and others.

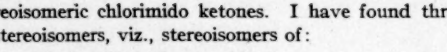
stereoisomeric chlorimido ketones. I have found three pairs of stereoisomers, viz., stereoisomers of:

(*a*) Chlorimido-*p*-chlorbenzophenone,

(*b*) Chlorimido-*p*-methoxybenzophenone,



and (*c*) Chlorimido-*p*-chlor-*p*-methoxybenzophenone,



In each case the structural identity of the α and β forms was established by converting each, by dry hydrogen chloride, into the hydrochloride of an imidobenzophenone, which gave with water the same ketone; a mixture of the ketone obtained from the α and that obtained from the β varieties melted at the same point as either separately. The reactions are:

and

That the two forms of a pair are not crystal or physical modifications is shown by the facts that each form has its own characteristic solubility, each form is recovered unchanged from its solutions, from its liquid form, when fused, and from its vapors—even in the presence of added crystals of the other form.[1] Further, each form persists even up to a temperature of 100°, and a mixture of approximately equal quantities of the two forms invariably melts lower than either form alone. One determination of the molecular weight

[1] *Vide* Stieglitz and Earle and Hilpert: *Loc. cit.*

of the higher melting of a pair of stereoisomers was made, namely of the α form of chlorimido-*p*-methoxybenzophenone; the higher melting form should, in case of polymerization of either form, be the polymer. The molecular weight determination showed it to have the normal molecular weight for a nonpolymerized body.[1]

The change of one stereoisomer into another was observed only once; the lower melting (β) form of chlorimido-*p*-chlorbenzophenone was found, after being kept for three months during a very hot summer, to have become completely converted, spontaneously, into the higher melting, stable or α form. Efforts to induce the same change by artificial means, e. g., by treatment of the two forms with chlorine, were not successful, the stereoisomers being unusually persistent, as compared with the chlorimido esters.[2] It may be recalled here that Hantzsch also found the stereoisomeric hydrazones of these ketones to be extremely stable, resisting transformation into each other by the agents which are usually successful.[3]

The stereoisomeric chlorimido ketones, thus far, have not given the slightest indication of suffering the "Beckmann rearrangement" which they were supposed to undergo so readily by those who had assumed them as intermediate products in the action of phosphorus pentachloride on ketoximes. They can be heated to 100° a short time without undergoing any such rearrangement. It is quite obvious, then, that the view that they form such intermediate products is now wholly untenable.

EXPERIMENTAL PART

Chlorimidobenzophenone, $(C_6H_5)_2C : NCl$.—The first chlori-

[1] Stieglitz and Earle and Hilpert carried out molecular weight determinations for both stereoisomers of a number of pairs of stereoisomeric chlorimido esters and in every case found the molecular weight of each form normal.

[2] *Vide* Stieglitz, Hale and Hilpert.

[3] By way of the return to the imidohydrochloride of the chlorimido-*p*-chlorbenzophenone, the α form was, by subsequent conversion back into a chlorimide, converted into a mixture of the α and β forms—this process being an aid in the preparation of pure material (the hydrochloride of the imidobenzophenone) for the formation of the chlorimides. As the higher melting α form is always obtained in large excess, the circle enables one to use the material over and over again to accumulate the lower melting β modification. These reactions, while proving the structural identity of the stereoisomers, do not accomplish any direct change of one stereoisomer into the other.

mide prepared was that of benzophenone. Here, of course, no stereoisomers were expected, but the work was done for the purpose of developing a good method for preparing chlorimido ketones. Benzophenone was prepared according to the Friedel and Crafts[1] reaction and converted into benzophenone dichloride by means of phosphorus pentachloride according to Kekulé and Franchimont's[2] directions. Benzophenone imidohydrochloride was prepared from the dichloride with the aid of urethane by the method of Hantzsch and Kraft,[3] a yield of forty-two per cent. of the theoretical being obtained. The best yield was obtained when three molecules of urethane were heated with one molecule of benzophenone dichloride. The reaction is a very slow one when carried out at 140°, but the product turns brown, indicating a decomposition, if the temperature is raised much higher. At this temperature the mass gives off gases (carbon dioxide and alkyl chloride) and crystallizes very slowly, and at least three hours are required for completion of the action. Longer heating does not increase the yield.

The chlorimide of benzophenone was prepared from the imidohydrochloride by treatment of the base with hypochlorous acid, much in the same way as the chlorimido esters are prepared. The action is represented by the equation

$$(C_6H_5)_2C : NH + HOCl \longrightarrow (C_6H_5)_2C : NCl + H_2O$$

The hypochlorous acid was prepared from sodium carbonate according to the directions of Erlenmeyer and Lipp.[4] A solution of two equivalents of the acid was prepared and one equivalent of potassium bicarbonate added to it. Then, while the solution was at freezing temperature, the solid imidohydrochloride was added. For instance, 8.5 grams of the hydrochloride was added to a mixture of 4 grams of potassium bicarbonate and of hypochlorous acid (prepared from 17 grams of dry sodium carbonate dissolved in 250 cc. of water and 11.5 grams of chlorine).[5] The solution became milky as

[1] Ann. chim phys., [6] **31,** 510.
[2] Ber. d. chem. Ges., **5,** 909 (1873).
[3] *Ibid.*, **24,** 3516 (1891).
[4] Ann. Chem. (Liebig), **219,** 185 (1883).
[5] Graebe: Ber. d. chem. Ges., **35,** 2750 (1902).

the imidohydrochloride dissolved, and a solid gradually crystallized out. After about ten minutes, during which the mixture was shaken constantly in the freezing bath, chloroform was added to dissolve the crystals. The two layers were separated by means of a separatory funnel, the stoppers of which were carefully greased to prevent any scratching. This precaution was deemed necessary because some nitrogen trichloride was liable to be produced in the reaction and the pungent odor of the mixture indicated its presence.

On evaporation of the chloroform, a yellowish crystalline mass was left. This mass was purified by crystallization from chloroform and ligroin and by recrystallization from warm ligroin. A yield of chlorimide representing seventy per cent. of the theoretical was thus obtained. The melting point of the crystals was 37°. The chlorimidobenzophenone thus obtained, when treated with potassium iodide in acid solution, sets iodine free quantitatively according to the equation

$$(C_6H_5)_2C : NCl + 2HI = (C_6H_5)_2C : NH_2Cl + 2I$$

This was used as a means of analysis, the iodine set free being titrated with sodium thiosulphate.

0.1872 gram substance gave 0.0308 gram chlorine.

	Calculated for $C_{13}H_{10}NCl$	Found
Cl	16.44	16.46

The chlorimide (0.4 gram) was dissolved in 25 cc. of ligroin, and dry hydrogen chloride was passed into the solution; a fine white precipitate resulted which analysis proved to be the regenerated imidohydrochloride.[1] The yield was quantitative. Analysis of it, by the silver nitrate method, gave the following results:

0.0776 gram substance gave 0.0128 gram chlorine.

	Calculated for $C_{13}H_{12}NCl$	Found
Cl	16.30	16.49

Treatment of the imidohydrochloride with hot water gave ben-

[1] *Vide* the equation, page 328.

zophenone quantitatively.[1] That the substance thus obtained was the ketone was proved by the fact that it melted at 46°, the melting point of synthetically prepared benzophenone, and when it was mixed with the synthetic product its melting point was not depressed.

Hydrochloride of Imido-p-chlorbenzophenone, $C_6H_5—C(:NH_2Cl)—C_6H_4Cl$.—Chlorimido-*p*-chlorbenzophenone was prepared in the same way as chlorimidobenzophenone, starting from *p*-chlorbenzophenone. This ketone was prepared according to Hantzsch and Kraft's[2] directions, and when treated with phosphorus pentachloride according to Overton's[3] method it gave *p*-chlorbenzophenone dichloride. Fractionation of the dichloride was carried out in a Brühl apparatus, the pure substance distilling at 192° under 12 mm. pressure. A yield of 88 per cent. of the theoretical was thus obtained.

To prepare *p*-chlorbenzophenone imidohydrochloride one molecule of *p*-chlorbenzophenone dichloride was mixed with three molecules of urethane and the whole heated to 140°–160° on the metal bath until the entire mass solidified. This was then extracted four times with benzene to free it from unchanged urethane and *p*-chlorbenzophenone which is formed. Recrystallization, by dissolving the crude residue in chloroform and precipitating with ligroin, gave the pure white hydrochloride. Owing to its difficult solubility in chloroform, it was found impractical to use this method for the purification of large quantities of material. I found that the imidohydrochloride did not need to be purified before conversion into the chlorimide. More nitrogen trichloride was formed, but this did not interfere with the work, and is not dangerous if the stopcocks are kept well greased with vaseline. The chlorimide could then be converted back into the imidohydrochloride quantitatively by the use of hydrogen chloride. This was found to be an easier method of preparing the pure imidochloride than the method of precipitation spoken of above, and it was used exclusively after the first preparation. A yield of 53 per cent. of the theoretical was obtained of the

[1] *Vide* the equation, page 328.

[2] *Loc. cit.*

[3] Ber. d. chem. Ges., **26**, 28 (1893).

crude material, and this was reduced to 42 per cent. in passing through the chlorimide. Analysis of the pure substance gave the following results:

0.1172 gram substance gave 0.0167 gram Cl, and 0.1224 gram substance gave 0.0175 gram Cl.

	Calculated for $C_{19}H_{11}NCl_2$[1]	Found I	Found II
Ionizable Cl	14.09	14.24	14.30

Stereoisomeric Forms of Chlorimido-p-chlorbenzophenone, $C_6H_5—C(NCl)—C_6H_4Cl$ and $C_6H_5—C(ClN)—C_6H_4Cl$.—α- and β-*p*-Chlorbenzophenone chlorimide were prepared from *p*-chlorbenzophenone imidohydrochloride by treatment with hypochlorous acid. A solution of two equivalents of hypochlorous acid was prepared as described above and the solid imidohydrochloride added to it. When the crude salt, containing ammonium chloride, was used much effervescence occurred. Great care had to be taken in handling the product, owing to the formation of nitrogen trichloride. No explosions ever did occur, but chemists trying the method must work very cautiously. After the imidohydrochloride was added, the flask was shaken vigorously in the freezing mixture for about ten minutes. The mixture was then extracted with very little chloroform and the chloroform solution drawn off in a separatory funnel. The chloroform was evaporated by a blast of air, a semisolid mass being left. This was extracted with warm ligroin. A solution of a mixture of the two forms of the chlorimide was thus obtained (about 80 per cent. of the theoretical yield). The two forms were separated as follows: Crystals obtained by cooling the ligroin extract were dissolved in as little chloroform as possible and about four volumes of ligroin added. This precipitated a mass of crystals which melted at 101°–102°. Recrystallization from warm ligroin raised their melting point to 104°. This form of the compound is called the α form. It appears in thin plates.

[1] Only the ionizable chlorine is determined, the method used being the titration of the salt with silver nitrate.

The chloroform-ligroin filtrate was then cooled to about —10° for a few minutes. Crystals melting at 46°–48° separated out. On repeated crystallization of this product from ligroin its melting point was finally raised to 55°. This form of the compound is called the β form. It appears as thin prisms or needles. Analysis of the two varieties by the potassium iodide method gave the following results:

0.1592 gram of the α form gave 0.0225 gram active chlorine and 0.1190 gram gave 0.0168 gram active chlorine.

	Calculated[1] for $C_{13}H_9NCl_2$	Found	
		I	II
Active Cl	14.18	14.14	14.12

0.1274 gram of the β form gave 0.01817 gram active chlorine and 0.0940 gram gave 0.0136 gram active chlorine.

	Calculated for $C_{13}H_9NCl_2$	Found	
		I[2]	II[2]
Active Cl	14.18	14.26	14.45

The identity of the structure of the two compounds was proved by converting them both into the imidohydrochloride and then into the ketone as follows:[3]

Three-tenths gram of the pure α form was dissolved in about 25 cc. of ligroin and dry hydrogen chloride passed into the solution to saturation. The imidohydrochloride was thus precipitated. The ligroin was decanted and the last traces blown off by a blast of air. Then the salt was treated with warm water. This gave 0.223 gram (89 per cent. of the theoretical yield) of the ketone, melting at 75°.5–76°. Mixtures of this substance with the synthetically prepared ketone and with the ketone obtained from the β form melted at the same temperature.

Three-tenths gram of the pure β form was treated in the same way and gave 0.230 gram of the same ketone as was obtained from the α form.

[1] Only one of the two chlorine atoms is determined, it alone being active toward the hydroiodic acid which was used in the analysis.

[2] In the preliminary report by Stieglitz and Peterson, as the result of errors in calculation 14.19 and 13.97 per cent. was reported.

[3] See page 328.

These experiments show conclusively that the substances are not structural isomers and are the same except in the configuration of the radical (: NCl).

The following experiments were carried out to exclude the possibility of crystal isomerism. One-tenth gram of the α form was heated to 120° and cooled slowly. At 85° solidification took place very rapidly. One-tenth gram of the β form was heated to 60°, then cooled to 45° and kept at that temperature for some time. No crystals separated out until inoculated with α or β crystals. The melting point was then found to be 54°; 55° is the melting point of the purest β form. A trace of the β form probably was in the α material and caused crystallization. The melting point shows that the substance persisted in the β form. One-tenth gram of each form was then brought into solution, separately, so that each solution was saturated at 25°. Cooling of the solutions then gave only the crystals from which the solutions were originally made, as melting point determinations proved. The crystals were again brought into solution, the solutions supercooled and inoculated with crystals of the other variety. Again, nothing but the crystals from which the solutions were originally made were obtained, as proved by their melting points and habit.

Hydrochloride of Chlorimido-p-*methoxybenzophenone*, $C_6H_5C(:NH_2Cl)C_6H_4OCH_3$.—*p*-Methoxybenzophenone was prepared according to the method of Gattermann, Ehrhardt, and Maisch.[1] The first preparation was made from anisyl chloride and benzene, but the yield was small. Benzoyl chloride and anisole gave, by the same treatment, almost a quantitative yield. This method was therefore used in subsequent preparations. It was found best to dissolve one equivalent of benzoyl chloride in ten times its volume of carbon disulphide and to add aluminium chloride to the mixture in about the same weight as the benzoyl chloride. A little more than one equivalent of anisole was then allowed to run slowly from a dropping funnel into the mixture. The reaction was complete as soon as all the anisole had been added. The carbon disulphide

[1] Ber. d. chem. Ges., **23**, 1204 (1890).

was then distilled off, the aluminium chloride decomposed with water acidulated with hydrochloric acid, and the ketone extracted with ether. Recrystallization from high-boiling ligroin was the best method found for the purification. The pure substance melted at 62°.

The ketone dichloride was obtained by the Hantzsch and Kraft[1] method, except that it was not purified. It was found that purification was not necessary before treatment with urethane. The excess of phosphorus pentachloride and the phosphorus oxychloride were distilled off in a vacuum at about 100°. The residue was treated directly with urethane. This gave an impure hydrochloride which could be readily purified. For instance, 20 grams of *p*-methoxybenzophenone and 20 grams of phosphorus pentachloride were heated in a flask on a metal bath to 140°–160° for three hours. The phosphorus oxychloride was then distilled off in a vacuum. The residue was treated with 18 grams of urethane and the temperature again raised to 160° for several hours. The viscous mass thus obtained was extracted several times with benzene to remove any urethane, ketone and dichloride. A white solid remained. The crude yield was 17 grams, or 73 per cent. of the theoretical. The substance melted above 170° with decomposition. When treated with warm water it gave a substance melting at 55°–58°, which, when mixed with synthetically prepared ketone (melting at 62°), melted a little higher than before. These facts indicated that the substance was impure imidohydrochloride of *p*-methoxybenzophenone. The hydrochloride was obtained in a pure state by converting the crude salt into the corresponding chlorimide, which by treatment with hydrogen chloride in ligroin solution forms the imidohydrochloride again. The analysis of the salt, purified in this way, gave the following results:

0.2390 gram substance gave 0.0339 gram chlorine.

	Calculated for $C_{14}H_{14}ONCl$	Found
Cl	14.48	14.19

[1] *Loc. cit.*

The salt is decomposed into the ketone (melting at 62°) and ammonium chloride on treatment with water.

Stereoisomeric Chlorimides of p-*Methoxybenzophenone*, $C_6H_5—\underset{\underset{NCl}{\|}}{C}—C_6H_4OCH_3$ and $C_6H_5—\underset{\underset{ClN}{\|}}{C}—C_6H_4OCH_3$.—The chlorimides of *p*-methoxybenzophenone were obtained from the impure imidohydrochloride by treatment with hypochlorous acid. A solution of hypochlorous acid was prepared in the same way as described for the preparation of benzophenone chlorimide, and the solid imidohydrochloride of *p*-methoxybenzophenone was added to the solution. When three equivalents of hypochlorous acid were used the product was gummy and hard to handle. When only two equivalents were used, the product was crystalline and gave a higher yield of the low-melting variety of the chlorimide, the one which is the more difficult to isolate. Use of the pure imidohydrochloride gave a still more satisfactory result. The rapid evaporation of the chloroform used for extracting the chlorimides from the hypochlorous acid solution also seemed to give a larger yield of the low-melting variety. In one preparation 10 grams of imidohydrochloride was treated with the equivalent of two molecules of hypochlorous acid. The chlorimides were extracted with chloroform and the chloroform evaporated rapidly by a blast of air. The mass was fractionated by dissolving it in as little chloroform as possible and reprecipitating part of the solid with about four volumes of ligroin. This gave a substance consisting almost entirely of the α variety. After several precipitations from chloroform by ligroin and recrystallizations from warm ligroin alone, the true melting point of the α variety was found to be 90°. These crystals were thin, six-sided plates. The first chloroform-ligroin filtrate from the precipitate of the α form was cooled to —10° and the beaker scratched. Fine white crystals came out; they were found to melt at 40°–42°. These crystals were dissolved in ligroin in the proportion of 1 gram of crystals to 25 cc. of ligroin and the solution set in the ice box for two days in a stoppered bottle. One very large asymmetric crystal of the β form and

several flat ones of the α variety appeared and could be easily separated mechanically. The melting point of the large crystal was found to be 54°, which was taken as the true melting point of the β form. A mixture of the two forms melted at 40°, which is far below the melting point of either form alone. Analysis gave the following results:

0.1249 gram of the α form gave 0.0177 gram chlorine and 0.1792 gram gave 0.0254 gram chlorine.

	Calculated for $C_{14}H_{12}ONCl$	Found	
		I	II
Cl	14.44	14.15	14.19

0.1363 gram of the β variety gave 0.0198 gram of chlorine.

	Calculated for $C_{14}H_{12}ONCl$	Found
Cl	14.44	14.52

Conversion of the chlorimides back into the imidohydrochloride and the ketone, similar to that carried out with the stereoisomers of chlorimido-*p*-chlorobenzophenone, was effected as follows: 0.335 gram of the α form was dissolved in chloroform and ligroin and dry hydrogen chloride passed into the solution to saturation. A yellow, sticky mass which smelled strongly of chlorine separated out. The filtrate was evaporated and gave but a small residue. Treatment of the mass with warm water dissolved it, and when the solution cooled a white crystalline solid, *p*-methoxybenzophenone, separated out. After about two hours the crystals were collected on a filter and dried on a clay plate. A yield of 0.263 gram of the ketone, or 83 per cent. of the theoretical, was obtained. Its melting point was found to be 59°.5–60°. Then 0.259 gram of the β form was subjected to the same treatment. A yield of 0.200 gram of the same ketone, or 89 per cent. of the theoretical, was obtained. The ketone obtained from the β form, and mixtures of this ketone with the preparation obtained from the α form and with synthetically prepared *p*-methoxybenzophenone, all melted at 59°–60°. There can be no question, therefore, of the identity of the structure of the two chlorimides.

Attempts to convert either variety of the chlorimide directly[1] into the other were made but without success. First 1.5 grams of the substance was heated to 100° for three hours. Its melting point was thereby lowered from 90° to 85°–87°. A mixture of the product with some pure α form melted at 88°–89°. Consequently very little transformation, if any, took place even at 100°. Then 0.1 gram of the β form was heated in the same manner; the melting point of the substance was lowered from 54° to 47°. A very small proportion of α form mixed with the β form lowers the melting point of the latter to 40°. There could have been very little change, therefore, if any, of the β into the α form. Finally 0.1 gram of the substance was heated for three hours in an atmosphere of dry chlorine[2] in a sealed tube. The mass became gummy, and after having been crystallized from chloroform, decomposed slightly at 175° but did not melt. Some transformation must have occurred, but not the transformation into the α form. The investigation of this reaction will be continued.

The molecular weight of the α form was determined by the cryoscopic method: 0.0903 gram substance dissolved in 11.58 grams benzene lowered the freezing point 0°.1675; 0.4791 gram in 11.58 grams benzene lowered the freezing point 0° 835.

	Calculated for $C_{14}H_{12}NOCl$	Found I	Found II
Mol. wt.	242.5	246.8	262.6

The theoretical constant, 53, for the lowering of the freezing point of 100 grams of benzene by one gram molecule of solute was used, as in previous determinations with chlorimido esters. The experimental constant, 49, would give the weights 226.5 and 238.

p-*Chlor*-p-*methoxybenzophenone*, $ClC_6H_4—CO—C_6H_4OCH_3$.— The method used for the preparation of *p*-methoxybenzophenone was also used for the preparation of *p*-chlor-*p*-methoxybenzophenone. Thirty-two grams of dry aluminium chloride

[1] Indirectly the two forms may be converted into each other by treatment with hydrogen chloride and subsequent change of the regenerated hydrochloride of the imidomethoxybenzophenone into the chlorimides by means of hypochlorous acid.

[2] Chlorine effects the reversible change of the labile stereoisomers of the chlorimido esters into the stable forms.

was pulverized in a hot mortar and added to a mixture of 100 cc. of carbon disulphide and 32 grams of freshly distilled *p*-chlorbenzoyl chloride.[1] The mixture was then cooled to 0° and kept at that temperature during the addition of twenty grams of anisole. The anisole was added very slowly, only one or two grams at a time, and the mixture was well shaken between the additions. Hydrogen chloride escaped very regularly. When the action ceased at this temperature, the mixture was allowed to warm up to room temperature. The carbon disulphide was distilled off and a mixture of ice and water, acidulated with hydrochloric acid, was added to the residue to decompose the aluminium chloride. During this operation the flask was kept in an ice-salt mixture. The gummy mass resulting was extracted with benzene, and the solution shaken five times with sodium hydroxide to remove any *p*-chlorbenzoic acid. The benzene was then evaporated and the residue crystallized from hot alcohol as follows: The whole mass was dissolved in the least possible quantity of boiling alcohol and then the solution was cooled. Thirty-two and a half grams of crystals separated out. The filtrate was added to an equal volume of cold water. A further precipitation occurred. This fraction was then crystallized from alcohol. The entire yield was 37 grams, or 82 per cent. of the theoretical. The melting point is 125°. Analysis of the substance gave the following results:

0.2323 gram substance gave 0.5797 gram CO_2 and 0.0980 gram H_2O.

	Calculated for $C_{14}H_{11}O_2Cl$	Found
C	68.18	68.06
H	4.49	4.69

Hydrochloride of Imido-p-chlor-p-methoxybenzophenone, $ClC_6H_4—C(:NH_2Cl)—C_6H_4OCH_3$.—This was prepared from the ketone as follows: *p*-Chlor-*p*-methoxybenzophenone was heated with one equivalent of phosphorus pentachloride on the metal bath to 160° for three hours. The phosphorus oxychloride was then distilled off in a vacuum at a temperature

[1] This was prepared from Kahlbaum's *p*-chlorbenzoic acid, melting at 237°.

of about 100°. Without further purification this crude product was dissolved in chloroform, and ammonia, dried over sodium hydroxide, run into the solution to saturation. A fine white mass, which was mainly ammonium chloride, separated out. This was filtered off and dry hydrogen chloride run into the filtrate to saturation. A yellowish precipitate was thrown down. The chloroform was decanted and the precipitate washed several times with chloroform and finally with ligroin. It was then dried in a vacuum over paraffin. The substance thus obtained gave low values for chlorine content for the hydrochloride of imido-*p*-chlor-*p*-methoxybenzophenone, but its behavior leaves no doubt that it consists chiefly of this salt, in an impure condition. From 10 grams of *p*-chlor-*p*-methoxybenzophenone 0.5 gram of the crude product was obtained. Water decomposes it into ammonium chloride and *p*-chlor-*p*-methoxybenzophenone (melting point 122°, which was raised somewhat by the admixture of the pure ketone, melting at 125°).

Treatment of the crude salt with hypochlorous acid converts it into the corresponding chlorimide, which is described below. It was expected that the latter would be converted by hydrogen chloride back into the hydrochloride of the imide, but contrary to expectations and to the behavior of other chlorimides, the chlorimide of *p*-chlor-*p*-methoxybenzophenone did not form a *pure* imidohydrochloride when treated with hydrogen chloride. The following analysis was obtained for the crude product prepared by the action of ammonia on the ketone dichloride:

0.2816 gram substance gave 0.0296 gram chlorine.

	Calculated for $C_{14}H_{13}ONCl_2$	Found
Cl	12.57	10.54

The behavior of the salt towards water agrees with the structure assigned to it, and the preparation of pure chlorimides from it (see below) confirms this structure. The preparation of the hydrochloride by this method is considered interesting, as it is the first instance of the formation of an imidohydrochloride from the aromatic ketone dichlorides by the direct

action of ammonia. Hantzsch showed that under the most varied conditions benzophenone dichloride would not form the imido hydrochloride with ammonia, and had to have recourse to the use of urethane with the dichloride in order to prepare the salt. I obtained exactly the same results on repeating Hantzsch's work with benzophenone dichloride.

Stereoisomeric Chlorimides of p-*Chlor*-p-*methoxybenzophenone*, $ClC_6H_4—\underset{\|}{\overset{NCl}{C}}—C_6H_4OCH_3$ and $ClC_6H_4—\underset{\|}{\overset{ClN}{C}}—C_6H_4OCH_3$.—The crude hydrochloride of imido-*p*-chlor-*p*-methoxybenzophenone (5 grams) obtained in the previous experiment was treated with the equivalent of two molecules of hypochlorous acid in the same way that the other chlorimides were prepared. This gave 3.5 grams of a mixture of α- and β-chlorimides, a yield of 70 per cent. of the theoretical. The product was extracted with about 25 cc. of cold ligroin (40°–60°). The solution was cooled to —20° and gave 1.4 grams of a substance melting at 50°–52°. This was again dissolved in ligroin and the solution set in the ice box in such a manner as to allow a very slow evaporation of the ligroin. Large crystals, mixed with some flat plates of the α variety, came out. The large crystals were recrystallized several times from ligroin before a substance was obtained which gave a sharp melting point, 65°, the highest melting point obtained for this form, the β variety. The residue from the first ligroin extraction was recrystallized from boiling ligroin (boiling at 70°–80°) several times and finally gave the pure α form with a melting point of 94°.5. Melting points of the two varieties and of mixtures of them were taken simultaneously and gave the following results: β form, 64°; α form, 94°; mixture, 50°–52°.

Analysis of the two varieties showed the following: 0.1778 gram of the α form gave 0.0227 gram active chlorine, and 0.1131 gram of the β form gave 0.01442 gram active chlorine.

	Calculated[1] for $C_{14}H_{11}ONCl_2$	Found	
		α	β
Active Cl	12.66	12.75	12.75

[1] Only the chlorine in the (: NCl) group is indicated by the analysis, which was made with the aid of potassium iodide.

The same kind of evidence as was used with the other stereoisomeric chlorimides was brought to exclude crystal and structural isomerism. After melting, each substance crystallizes again in its own characteristic form, even when it has been heated several degrees above the melting point of the higher-melting form. When the substances are mixed with each other the melting point is decidedly depressed, as shown above. And, finally, each substance crystallizes in its own form from a solution of a mixture of the two. These facts exclude crystal isomerism.

The stereoisomeric chlorimidoketones were converted back into the ketone in the usual way in order to exclude the possibility of structural isomerism. The results follow: 0.266 gram of the α form was dissolved in chloroform and the solution saturated with dry hydrogen chloride. This treatment produced a white precipitate. Ligroin was then added to complete the precipitation. The chloroform-ligroin mixture was decanted and the last traces of the solvent blown off in a blast of air. The residual salt was dissolved in hot water and gave 0.216 gram of *p*-chlor-*p*-methoxybenzophenone (melting at 124°–124°.5). This is a yield of 92 per cent. of the theoretical. A mixture of the product with the ketone obtained in the same way from the β form melted at the same point and a mixture with synthetically prepared ketone (melting at 125°) melted at 125°. When 0.173 gram of the β form was treated by the same process 0.134 gram, or 90 per cent. of the theoretical weight of ketone (melting at 125°), was obtained.

Attempts to prepare chlorimido-*p*-nitrobenzophenone and chlorimido-*p*-methoxy-*o*-chlorbenzophenone had to be given up as a result of difficulties experienced in preparing the corresponding imidohydrochlorides of the two ketones. A chlorimide of *p*-methylbenzophenone was prepared but not investigated further when it was found that the lower melting of the two stereoisomers, if present at all, formed an oil difficult to purify. A crystalline compound, presumably the higher melting stereoisomer, was not specially purified and melted between 35° and 45°; it contained 14.62 per cent.

of chlorine, while a compound $CH_3C_6H_4C(:NCl)C_6H_5$ would demand 15.44 per cent. There is no doubt that such a chlorimide may be prepared, but since the main object of this investigation was to isolate well-defined stereoisomeric compounds, the product was not further investigated. The oil, according to the analytical results, was not a pure compound, but contained some chlorimide.

o-*Chlor*-p-*methoxybenzophenone*, $ClC_6H_4.CO.C_6H_4OCH_3$. — In the attempt to prepare *o*-chlor-*p*-methoxybenzophenone chlorimide, *o*-chlor-*p*-methoxybenzophenone was obtained from *o*-chlorbenzoyl chloride and anisole. Since it has not been described in the literature, its preparation will be briefly discussed here. Twenty-five grams of *o*-chlorbenzoyl chloride was dissolved in 100 cc. of carbon disulphide and 25 grams of dry powdered aluminium chloride was added to the solution. The mixture was then cooled in a freezing mixture and the equivalent of one molecule of anisole allowed to drop into it slowly from a dropping funnel. Hydrogen chloride was given off regularly and a crystalline body separated out. The carbon disulphide was then distilled off and the aluminium chloride decomposed by water acidulated with hydrochloric acid. The residue was extracted with ether and the extract well washed with sodium hydroxide to free it from any *o*-benzoyl chloride. The ether was then distilled off and the residue fractionated in a Brühl apparatus at reduced pressure. The pure substance distilled at 250° under 50 mm. pressure. Analysis of it shows the following results:

0.1553 gram substance gave 0.3865 gram CO_2 and 0.0680 gram H_2O.

	Calculated for $C_{14}H_{11}O_2Cl$	Found
C	68.18	67.90
H	4.49	4.90

In conclusion, I wish to express my gratitude to Professor Stieglitz for his kind guidance and for the inspiration he has given me.

[Contributions from the Sheffield Laboratory of Yale University]

CXCIII—RESEARCHES ON PYRIMIDINES
THE CONDENSATION OF ETHYL FORMATE AND DIETHYL OXALATE WITH SOME PYRIMIDINE-THIOGLYCOLLATES

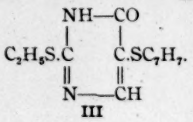
[FIFTY-THIRD PAPER]

By Treat B. Johnson and Norman A. Shepard

This paper is a contribution to our knowledge of the chemical behavior of the *thioglycollide* grouping —S.CH_2.CO—. The study of this grouping is one of a projected series on organic sulphur combinations which has been planned for this laboratory.

In a previous publication, Johnson and Guest[1] have shown that ethyl formate condenses in ether with ethyl benzylthioglycollate (I), in the presence of sodium, forming the sodium salt of ethyl α-benzylmercapto-β-hydroxyacrylate (II). This ester (II) condensed, in an alkaline solution, with pseudoethylthiourea, $NH:C(SC_2H_5)NH_2$, giving a representative of a new class of mercaptopyrimidines in which a mercapto group is linked to the 5-position of the pyrimidine ring, viz., 2-ethylmercapto-5-benzylmercapto-6-oxypyrimidine (III). The action of diethyl oxalate on this thioglycollate (I) was not examined.

$$\underset{\text{I}}{C_6H_5CH_2SCH_2COOC_2H_5} \xrightarrow{HCOOC_2H_5} \underset{\text{II}}{HOCH:C(SC_7H_7)COOC_2H_5} \longrightarrow$$

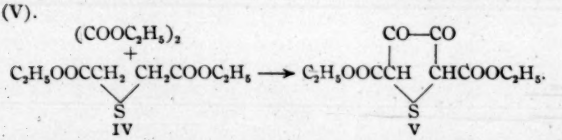


III

Recently Hinsberg[2] has observed that the methylene groupings in diethyl thiodiglycollate (IV) are also reactive towards

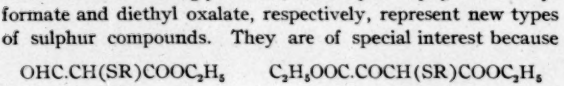
[1] This Journal, **42**, 271 (1909).
[2] Ber. d. chem. Ges., **43**, 901 (1909).

esters, in the presence of sodium. The thio compound condenses, for example, with diethyl oxalate, giving the cyclic compound α,α'- dicarbethoxy- β,β' - diketotetrahydrothiophene (V).



IV V

These ketone esters (VI and VII), which are formed by the condensation of thioglycollates, $RS.CH_2COOC_2H_5$, with ethyl formate and diethyl oxalate, respectively, represent new types of sulphur compounds. They are of special interest because



VI VII

of their possible use for further syntheses and their investigation is now in progress. We shall give a description of the chemical behavior of some of these condensation products in later papers.

It became apparent, after much preliminary experimental work, that the success of our research depended on the employment of thioglycollates which possessed certain characteristic properties. Thioglycollates, $RS.CH_2COOC_2H_5$, in which R was substituted by alkyl groups (C_6H_5, C_2H_5, etc.), were unsuitable because of the firm union between the alkyl group and the sulphur atom. Ethyl benzoylthioglycollate,[1]

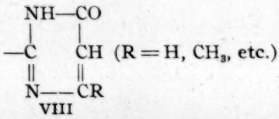
$$C_6H_5CO.SCH_2COOC_2H_5,$$

and other acylthioglycollates were then tried, but this class of esters was found to be too unstable because of the easy replacement of the acyl radicals by the action of alkali during the condensations. Furthermore, all the thioglycollates of both these types which were examined gave, on condensation with ethyl formate and diethyl oxalate, products which were

[1] Wheeler and Johnson: THIS JOURNAL, **26**, 198.

oils or low-melting solids possessing very unfavorable properties. They could not be purified by distillation, and moreover the yields were so small in most cases that they could not be prepared easily in sufficient amounts for synthetical work.

Efforts have therefore necessarily been made to find an organic grouping to substitute for R which would confer a crystalline character on the compounds under examination, and also could be removed easily from the sulphur by hydrolysis. We now find, after an examination of several groupings, that a 6-oxypyrimidine radical (VIII) fulfils all these conditions.



VIII

The only pyrimidinethioglycollate hitherto described in the literature is ethyl 6-oxypyrimidine-2-thioglycollate (XI), which Wheeler and Liddle[1] prepared by the action of ethyl chloracetate on the sodium salt of 2-thiouracil. We now find that this ester condenses with ethyl formate and diethyl oxalate in alcohol and in the presence of sodium ethylate, forming almost quantitatively ethyl 6-oxypyrimidine-2-(α-thio-β-hydroxyacrylate) (XII) and diethyl 6-oxypyrimidine-2-oxalthioglycollate (X), respectively. We have also prepared ethyl 4-methyl-6-oxypyrimidine-2-thioglycollate (XIV) by the action of ethyl chloracetate on 2-thio-4-methyluracil.[2] This new thioglycollate condensed as smoothly with ethyl formate and diethyl oxalate as the ester (XI) and formed ethyl 4-methyl-6-oxypyrimidine-2-(α-thio-β-hydroxyacrylate) (XV), and diethyl 4-methyl-6-oxypyrimidine-2-oxalthioglycollate (XVI), respectively. These four β-ketone esters (X, XII, XV and XVI) are crystalline compounds melting above 100°, and all possess physical properties which are very desirable for the

[1] This Journal, **40**, 547.

[2] List: Ann. Chem. (Liebig), **236**, 12 (1886). Wheeler and McFarland: This Journal, **42**, 105 (1909).

study of the chemical behavior of these types of sulphur compounds.

Ethyl 6-oxypyrimidine-2-(α-thio-β-hydroxyacrylate) (XII) condensed normally with thiourea, forming a representative of a new type of dipyrimidines, viz., 2-(2-thio-6-oxypyrimidine-5-mercapto)-6-oxypyrimidine (IX). A compound containing the same percentage of nitrogen and having nearly the same decomposition point as the dipyrimidine (IX) was also obtained by the condensation of the diethyl 6-oxypyrimidine (X) with thiourea. The yield, however, was so small that the identity of the two condensation products could not be accurately established. Ethyl 4-methyl-6-oxypyrimidine-2-(α-thio-β-hydroxyacrylate) (XV) condensed with thiourea, giving 2-(2-thio-6-oxypyrimidine-5-mercapto)-4-methyl-6-oxypyrimidine (XVIII), while diethyl 4-methyl-6-oxypyrimidine-2-oxalthioglycollate (XVI) reacted to form a dipyrimidine of unknown constitution. We have previously assigned to it the formula of a tricyclic compound (XVII). Work on the determination of the constitution of these condensation products of thiourea with the pyrimidine-2-oxalthioglycollates (X and XVI) is now in progress and the results will be published in a later paper.

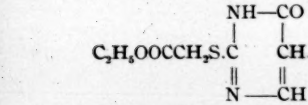
Especially interesting was the behavior of diethyl 6-oxypyrimidine-2-oxalthioglycollate (X) when digested with concentrated hydrochloric acid. Uracil was not formed as expected, but the ester underwent hydrolysis, giving an excellent yield of 6-oxypyrimidine-2-thiopyruvic acid (XIII). 6-Oxypyrimidine-2-thioglycollic acid undergoes hydrolysis under the same conditions, and even when boiled with water, giving uracil quantitatively.[1] Thiopyruvic acid, $HSCH_2COCOOH$, has not been described and this pyrimidine (XIII) should be of value for further interesting syntheses.

The various transformations described above are represented by the following structural formulas:

[1] Wheeler and Liddle: *Loc. cit.*

EXPERIMENTAL PART

Ethyl 6-Oxypyrimidine-2-thioglycollate,

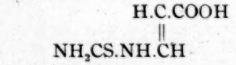


$C_2H_5OOCCH_2S.C$ CH.—This pyrimidine, which has been described in a previous paper,[1] is easily obtained by the action of ethyl chloracetate on thiouracil in the presence of alkali. To insure, however, a complete reaction it is necessary that the thiouracil be first completely converted into its sodium salt. Suspension of the pyrimidine in alcohol containing the required amount of sodium is not sufficient. Since both the pyrimidine and its sodium salt are practically insoluble in alcohol it is necessary to thoroughly shake the mixture and finally to warm it on the steam bath for a few minutes before adding the ethyl chloracetate. Fifty-two grams of 2-thiouracil were converted into its sodium salt by treatment with 9.6 grams of sodium dissolved in 310 cc. of absolute alcohol. Fifty-two grams of ethyl chloracetate were then added, in small portions, and the mixture digested on the steam bath until the solution gave an acid reaction, and then allowed to stand for 8–10 hours. The solution was then filtered to separate the sodium chloride which had deposited, and finally concentrated on the steam bath, when we obtained the thioglycollate. This was washed with cold water to remove traces of salt, and then purified by crystallization from alcohol or hot water. It separated in beautiful, prismatic crystals, which melted at 155° to a clear oil.

The solid material removed by filtration, which was chiefly sodium chloride, was triturated with water, when a crystalline substance was obtained insoluble in this solvent. It was also practically insoluble in alcohol but dissolved in boiling water and separated, on cooling, in glistening plates. The compound contained no inorganic material and after decolorization in hot water with bone charcoal it did not melt below 300°. It was also insoluble in dilute hydrochloric acid and

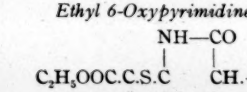
[1] **Wheeler and Liddle:** *Loc. cit.*

was not altered by digestion with this reagent. 2-Thiouracil decomposes at 340°. The compound contained sulphur, and nitrogen determinations agreed with the calculated value for thioureaacrylic acid. Because of its stability, in the presence of boiling hydrochloric acid, it was assigned the constitution of the *trans* modification of this acid, viz., trans-*β*-*thioureaacrylic acid*,



	Calculated for $C_4H_6O_2N_2S$	Calculated for $C_4H_4ON_2S$	Found I	Found II
N	19.17	21.87	18.78	19.19

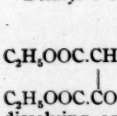
Ethyl 6-Oxypyrimidine-2-(α-thio-β-hydroxyacrylate),



—Seventy-four hundredths of a gram of sodium was dissolved in 20 cc. of anhydrous ethyl alcohol and 3.4 grams of ethyl 6-oxypyrimidine-2-thioglycollate dissolved in the cold solution. Two and four-tenths grams (2 mols.) of ethyl formate were then poured into the solution and the mixture allowed to stand at ordinary temperature for 3 days. No solid material separated and a transparent yellow solution was obtained. This was cooled to 0°, acidified with hydrochloric acid and the insoluble sodium chloride filtered off. When the alcohol filtrate was evaporated at ordinary temperature the above pyrimidine was obtained as a crystalline solid. A small amount of the same compound also separated with the sodium chloride and was recovered by trituration with water to dissolve the salt. This compound is very soluble in alcohol and difficultly soluble in cold water. It crystallizes from absolute alcohol in well developed prisms which melt at 138–140° to an oil with slight effervescence. A mixture of this pyrimidine and unaltered thioglycollate (melting at 155°) melted at 120–130°. The yield was good. Analyses (Kjeldahl):

	Calculated for $C_9H_{10}O_4N_2S$	Found I	Found II
N	11.57	11.03	11.16

Diethyl 6-Oxypyrimidine-2-oxalthioglycollate,



$C_2H_5OOC.CH.S.C$ CH.—This pyrimidine was prepared by

$C_2H_5OOC.CO$ N—CH

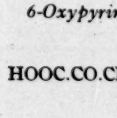
dissolving 15.0 grams of ethyl 6-oxypyrimidine-2-thioglycollate and 15.4 grams of diethyl oxalate in 58.0 cc. of cold absolute alcohol containing 3.3 grams of sodium in the form of sodium ethylate, and then allowing the solution to stand at ordinary temperature for several days (1 week). The solution was then acidified with hydrochloric acid, when this pyrimidine was deposited mixed with sodium chloride. After trituration with cold water to remove the salt it was obtained as a colorless crystalline solid which crystallized from hot alcohol in stout blocks. They melted at 171° to an oil and the yield was 17.5 grams. Analyses (Kjeldahl):

	Calculated for $C_{12}H_{14}O_5N_2S$	Found I	Found II
N	8.9	8.4	8.68

When the acid alcoholic filtrate (above) was allowed to evaporate at ordinary temperature more of this same pyrimidine was obtained, but mixed with another substance which did not contain sulphur. The latter compound dissolved in boiling water and separated on cooling in corpuscular crystals which did not melt or decompose below 300°. It was identified as uracil; it contained 24.5 per cent. of nitrogen, while the calculated is 25 per cent.

Action of Hydrochloric Acid on Diethyl 6-Oxypyrimidine-2-oxalthioglycollate

6-Oxypyrimidine-2-thiopyruvic Acid,



$HOOC.CO.CH_2S.C$ CH.—One gram of the above thiogly-

N—CH

collate was dissolved in 20 cc. of concentrated hydrochloric acid and the solution evaporated to dryness on the steam bath. The residue was redissolved in 15 cc. of acid and evaporated again, when we obtained an oily product which immediately solidified on triturating with alcohol. The crude substance decomposed at 180°–182° with effervescence, leaving a charred residue. It was purified by recrystallization from alcohol and separated in colorless crystals which began to darken at 190°–195° and then decomposed at 200°–201° with violent effervescence. It gave a strong test for sulphur. 6-Oxypyrimidine-2-thioglycollate[1] melts at 178° and is decomposed when boiled with water, giving uracil. It also crystallizes with one molecule of water. Our compound was anhydrous. The nitrogen determinations were high for the pyruvic acid, but this was very probably due to a trace of uracil which was present as impurity. The experiment was repeated and the same compound, melting at 200°–201°, was obtained. Analyses (Kjeldahl):

	Calculated for $C_7H_6O_4N_2S$	Found I	Found II
N	13.1	13.6	13.7

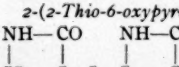
Action of Alkali on Diethyl 6-Oxypyrimidine-2-oxalthioglycollate.—Two grams of the pyrimidine and three molecular proportions of potassium hydroxide (1 gram) were dissolved in 5 cc. of water and the solution heated at 100° for one hour. After standing for 10–12 hours the solution was acidified with hydrochloric acid and evaporated to dryness. The residue was dissolved in boiling water and cooled, when uracil separated in characteristic, corpuscular crystals melting above 320°. Analyses (Kjeldahl):

	Calculated for $C_4H_4O_2N_2$	Found I	Found II
N	25.00	24.52	24.6

[1] **Wheeler and Liddle:** *Loc. cit.*

Condensation of Thiourea with Ethyl 6-Oxypyrimidine-2-(α-thio-β-hydroxyacrylate)

2-(2-Thio-6-oxypyrimidine-5-mercapto)-6-oxypyrimidine,



.—Two-tenths of a gram of sodium (2 mols.) were dissolved in 10 cc. of absolute alcohol and 0.9 gram of the formyl compound dissolved in the solution. Forty-two hundredths gram of finely pulverized thiourea was then added and the mixture heated on the steam bath for about one hour. The excess of alcohol was then expelled and a residue obtained which dissolved immediately in cold water. On acidifying the solution with hydrochloric acid no precipitate was obtained. An excess of a saturated mercury chloride solution was mixed with the solution and a small volume of dilute sodium hydroxide solution added, when we obtained a yellow, insoluble mercury salt. This was filtered off, washed with water, suspended in cold water and the mercury precipitated as mercury sulphide with hydrogen sulphide. After filtering from the mercury sulphide and concentrating the filtrate we obtained the above pyrimidine. It was very soluble in alcohol and hot water. It separated from a saturated aqueous solution in needles which shriveled when heated in a capillary tube and then decomposed with effervescence from 285°–295°, according to the rate of heating. It gave a strong test for sulphur. Analysis (Kjeldahl):

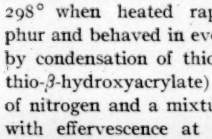
	Calculated for $C_8H_6O_2N_4S_2$	Found
N	22.04	22.11

Condensation of Thiourea with Diethyl 6-Oxypyrimidine-2-oxalthioglycollate.—Five grams of this pyrimidine were condensed with 2.4 grams of thiourea (2 mols.) by digestion in 35 cc. of alcohol with 0.72 gram of sodium in the form of sodium ethylate. After heating on the steam bath for two hours the alcohol was removed by evaporation and the resi-

due dissolved in water. On adding hydrochloric acid to this solution, and cooling to 0°, nothing separated. An excess of mercury chloride solution was then added, when we obtained an immediate precipitate of a dense yellow mercury salt. This was washed with water and decomposed in the usual manner with hydrogen sulphide and the aqueous filtrate, after separation of mercury sulphide, evaporated to dryness. We obtained a very small quantity of a crystalline product which was very soluble in water and hot alcohol. When recrystallized from 95 per cent. alcohol it separated in needlelike prisms which decomposed with effervescence at about 295°–298° when heated rapidly. The compound contained sulphur and behaved in every respect like the pyrimidine obtained by condensation of thiourea with ethyl 6-oxypyrimidine-2-(α-thio-β-hydroxyacrylate). It contained the same percentage of nitrogen and a mixture of the two compounds decomposed with effervescence at 290°–294°. Owing, however, to the indefinite melting point and the small quantity of this compound we were not able to establish accurately the identity of the two compounds. Its examination will be taken up again later. Analysis (Kjeldahl):

	Calculated for $C_5H_6O_2N_2S_2$	Found
N	22.04	21.85

Ethyl 4-Methyl-6-oxypyrimidine-2-thioglycollate,



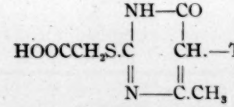
2-thio-4-methyl-6-oxy-pyrimidine which was used in this preparation was made by condensing thiourea with ethyl acetacetate in alcoholic solution.[1] Sixty-five grams of this thiopyrimidine were converted into its sodium salt by boiling for one-half an hour with 325 cc. of alcohol in which were previously dissolved 10.5 grams of sodium. Fifty-five and eight-tenths grams of ethyl chloracetate were then slowly added and the mixture

[1] Wheeler and McFarland: THIS JOURNAL, **42**, 105.

finally heated on the steam bath until the reaction was complete (1.5 hours). The chief amount of the above pyrimidine deposited, on cooling, with the sodium chloride and was separated from this impurity by trituration with cold water. The rest of the compound was obtained after evaporation of the alcohol filtrate. The pyrimidine is soluble in boiling benzene, alcohol and water. It was purified for analysis by recrystallization from 95 per cent. alcohol and separates from this solvent in colorless needles which melt at 145°–146°. The yield was 65 grams. Analyses (Kjeldahl):

	Calculated for $C_5H_{12}O_3N_2S$	Found I	Found II
N	12.28	11.92	11.96

4-Methyl-6-oxypyrimidine-2-thioglycollic Acid,



$HOOCCH_2S.C(NH{-}CO)=CH.(N{-}C.CH_3)$

—This acid was obtained in the form of its dipotassium salt by saponification of five grams of the preceding thioglycollate with 2.4 grams of potassium hydroxide in alcoholic solution. After heating on the steam bath for 1 hour and then cooling the salt separated in colorless crystals. Analysis (Kjeldahl):

	Calculated for $C_7H_6O_3N_2SK_2$	Found
N	10.1	9.62

The free acid was obtained by dissolving its potassium salt in cold water and then adding a slight excess of hydrochloric acid. It separated as a crystalline solid and crystallized from hot water in colorless prisms which melted at 192°–197° with effervescence. Analyses (Kjeldahl):

	Calculated for $C_7H_6O_3N_2S$	Found I	Found II
N	14.0	13.78	13.77

Ethyl 4-Methyl-6-oxypyrimidine-2-(α-thio-β-hydroxyacrylate), $C_2H_5OOC.C.S.C(NH{-}CO)(CH.)(HO.CH)(N{-}CCH_3)$.—Two grams of sodium and 10 grams of ethyl 4-methyl-6-oxypyrimidine-2-thioglycollate were dissolved in 40 cc. of cold absolute alcohol and then 6.5 grams of ethyl formate (2 mols.) were mixed with the solution. After allowing to stand at ordinary temperature for two days the solution was acidified with hydrochloric acid, filtered and then allowed to evaporate spontaneously in the air. We obtained a yellow, viscous substance which did not solidify until after long trituration with cold water. It was very soluble in 95 per cent. alcohol and separated, after the first crystallization, in colorless prisms melting at 75°–85°. After two further recrystallizations from this same solvent the melting point remained constant at 106°. Analyses (Kjeldahl):

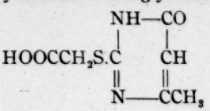
	Calculated for $C_{10}H_{12}O_4N_2S$	Found I	Found II
N	10.9	10.89	10.88

In a second experiment 4.0 grams of sodium were first dissolved in 80 cc. of absolute alcohol and then 20 grams of the thioglycollate and 13 grams of ethyl formate dissolved in the solution. The mixture was then allowed to stand, in a corked flask, for three weeks, when the excess of alcohol was removed by evaporation in a vacuum over concentrated sulphuric acid. We obtained the sodium salt of the condensation product as a lemon-yellow powder which became pasty on exposure to the air. Three grams of the salt were dissolved in a few cc. of water, cooled to 0° and hydrochloric acid added to the solution, when we obtained a light yellow oil which showed no signs of solidifying. The oil was separated and washed repeatedly with cold water and finally cooled to 0°. There was still no evidence of the oil solidifying after standing for several hours. The water was finally decanted and the oil dissolved in 95 per cent. alcohol and precipitated again by diluting the

alcohol with water. After standing a few minutes it then solidified and melted at about 85°. On recrystallizing from dilute alcohol the melting point was finally constant at 106°–108°.

The remainder of the above sodium salt was dissolved in cold water and the solution acidified with hydrochloric acid. The pyrimidine separated first as an oil which finally crystallized on long standing. It was purified by crystallization from alcohol and melted at 106°–108°. A small quantity of a difficultly soluble compound was separated here. It contained no sulphur, melted above 290° and was identified as 4-methyluracil.

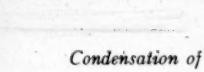
Attempt to Reduce Ethyl 4-Methyl-6-oxypyrimidine-2-(α-thio-β-hydroxyacrylate) with Sodium Amalgam.—Two and eight-tenths grams of the pyrimidine were dissolved in 75 cc. of 95 per cent. alcohol and a large excess of 2.5 per cent. sodium amalgam added to the solution. A few cc. of water were then added, the reaction allowed to proceed at ordinary temperature for a few hours and the mixture finally heated for four hours on the steam bath. The excess of alcohol was then removed by evaporation, the solution neutralized with hydrochloric acid, decanted from mercury and finally evaporated to dryness. We obtained a crystalline residue which was easily soluble in cold water. This was dissolved in dilute acetic acid and the solution allowed to stand, when colorless prisms separated which melted without further purification at about 192°–193° with effervescence. It crystallized from hot water in prisms melting at 193°–197° and was identified as 4-methyl-6-oxypyrimidine-2-thioglycollic acid,



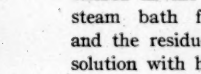
the formyl group of the original pyrimidine having been removed by the action of the alkali. Analysis (Kjeldahl):

	Calculated for $C_7H_8O_3N_2S$	Found
N	14.0	13.81

Condensation of Thiourea with Ethyl 4-Methyl-6-oxypyrimidine-2-(α-thio-β-hydroxyacrylate)

2-(2-Thio-6-oxypyrimidine-5-mercapto)-4-methyl-6-oxypyrimidine,  .—Seven grams of the sodium salt of ethyl 4-methyl-6-oxypyrimidine-2-(α-thio-β-hydroxyacrylate) were dissolved in 25 cc. of alcohol and condensed with 2.7 grams of thiourea in a manner similar to that described in the previous experiments. After heating on the steam bath for four hours, the alcohol was evaporated and the residue dissolved in cold water. On acidifying the solution with hydrochloric acid an orange powder separated. This substance melted at 145°–146° and was identified as the original thioglycollate. The filtrate was treated with an excess of mercury chloride solution, when an orange mercury salt deposited. This was decomposed in the usual manner with hydrogen sulphide, the mercury sulphide filtered off, and the filtrate evaporated to dryness. We obtained a crystalline substance, mixed with a little oil, which was purified by washing with cold alcohol and benzene to remove the oil and then crystallized from hot water. It separated in characteristic clusters of prisms which did not melt below 300°. Analysis (Kjeldahl):

	Calculated for $C_9H_8O_2N_4S_2.H_2O$	Calculated for $C_9H_8O_2N_4S_2$	Found
N	19.5	20.9	19.38

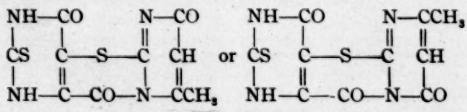
Diethyl 4-Methyl-6-oxypyrimidine-2-oxalthioglycollate,  .—Ten grams of ethyl 4-methyl-6-oxypyrimidine-2-thioglycollate were dissolved in 40 cc. of anhydrous ethyl alcohol and condensed with 9.6 grams of diethyl oxalate in the presence of sodium ethylate. After allowing the mixture to stand for 10 days the solution was al-

lowed to evaporate spontaneously to remove the excess of alcohol and then diluted with water and carefully acidified with hydrochloric acid. The above pyrimidine separated as a colorless, crystalline solid. It deposited from boiling alcohol in beautiful stout blocks which melted at 139°–140°. When mixed with unaltered material the melting point was lowered to 120°. Analyses (Kjeldahl):

	Calculated for $C_{13}H_{16}O_6N_2S$	Found I	Found II
N	8.54	8.66	8.51

When the acid filtrate (above) was allowed to stand a small quantity of 4-methyluracil separated.

Condensation of Thiourea with Diethyl 4-Methyl-6-oxypyrimidine-2-oxalthioglycollate.—Seven-tenths of a gram of sodium (2 mols.) was dissolved in 25 cc. of absolute alcohol and 5.0 grams of the above pyrimidine and 2.4 grams of thiourea dissolved in the solution. After allowing to stand for two days the solution was heated on the steam bath for two hours. A bright red, jellylike solution was obtained which deposited, on cooling, a small quantity of yellow, ragged prisms (thiourea). These were filtered off, the excess of alcohol removed by evaporation at 100°, and the product obtained dissolved in water. On cooling, a little unaltered pyrimidine separated, which melted at 145° after being crystallized from alcohol. The filtrate was treated with mercury chloride and sodium hydroxide, when a dense mercury salt deposited. This was decomposed as in the preceding experiments, the mercury sulphide filtered off, and the filtrate then evaporated to dryness. We obtained a crystalline substance which was purified by repeated crystallizations from 95 per cent. alcohol. It separated in hexagonal tables which shriveled at 140° and then melted at 164°–165°. Nitrogen determinations agreed with the calculated value for the two isomeric tricyclic derivatives



The study of these interesting compounds will be taken up later. Analyses (Kjeldahl):

	Calculated for $C_{10}H_6O_3N_4S_2$	Found I	Found II
N	19.0	18.94	18.84

NEW HAVEN, CONN.
July 20, 1911

REDUCTION OF MERCURIC CHLORIDE BY PHOSPHOROUS ACID AND THE LAW OF MASS ACTION

BY JAMES B. GARNER, JOHN E. FOGLESONG AND ROGER WILSON

In very recent years the velocities of a large number of chemical reactions have been studied in order to determine their conformity to the law of mass action. Many of these confirm the theory that the velocity of a reaction is a function of the number of molecules taking part in it, yet quite a number of notable exceptions have been discovered. In the greatest number of cases, reactions have been investigated which do not involve more than two or three molecules, since the chances of two or three molecules coming together in such a way as to produce chemical action are much greater than those of four or a larger number coming into a similar relation. It is true that many chemical reactions are represented as taking place between more than three molecules, yet a careful study of the velocity of these reactions in terms of the law of mass action reveals the fact that in many cases the reaction takes place in steps, or is complicated by side reactions until the usual simple mathematical expressions will not yield the results expected from the theory. In this way, however, the study of the velocity of reactions has been highly beneficial, because more light has been thrown upon the mechanism of the reactions themselves than could have been done by any other means.

The first reaction of the fourth order to be investigated was the interaction of bromic and hydriodic acids by Ost-

wald.[1] He found that the values of K obtained from the equation

$$K = \frac{1}{t}\left(\frac{x}{a(a-x)}\right)$$

were not constant, but continually decreased with the progress of the reaction. He did not attempt to find a solution for this behavior, however, as his purpose was to find the influence of certain acids upon the velocity of the reaction. This same reaction was later studied by Magnanini,[2] then by Noyes,[3] and finally by Judson and Walker.[4] It was shown by Noyes and by Judson and Walker that the reaction was one of the fourth order. Since that time a few reactions of this order have been investigated. Such are the action of heat upon potassium chlorate,[5] the reaction between chromic acid and phosphorous acid,[6] and the action of bromine upon benzene.[7]

These have shown that in general the number of molecules interacting determines the order of the reaction. The more favorable the conditions, the more nearly do the facts confirm the theory.

It has been noticed in the work in this laboratory that the action of phosphorous acid upon mercuric chloride proceeds very slowly in dilute aqueous solutions and at ordinary temperatures. It has therefore occurred to us that it might be of interest to determine the extent of the reaction, the effect of different temperatures and concentrations, and the order of the reaction.

It has been shown that in aqueous solutions at ordinary temperatures, mercurous chloride is precipitated as a white, granular precipitate and orthophosphoric acid and hydrochloric acid are formed. The reaction has been expressed by the equation

$$2HgCl_2 + H_3PO_3 + H_2O = 2HgCl + H_3PO_4 + 2HCl$$

[1] Z. physikal. Chem., **2**, 127 (1888).
[2] Gazz. chim. ital., **20**, 390.
[3] Z. physikal. Chem., **19**, 599 (1896).
[4] J. Chem. Soc., **73**, 410 (1898).
[5] J. Scobai: Z. physikal. Chem., **44**, 319 (1903).
[6] G. Viard: Compt. rend., **124**, 148 (1897).
[7] L. Bruner: Z. physikal. Chem., **41**, 513 (1902).

At higher temperatures the velocity of the reaction is greatly increased, and in addition to the precipitate of mercurous chloride there is a deposit of metallic mercury. It is now our plan to show that the above equation is an exact statement of the facts for aqueous solutions of varied concentrations of mercuric chloride and phosphorous acid at 25° and 30°.

Methods of Work

At first it was our endeavor to determine the temperature and concentrations at which the change took place to the best advantage, and to find the point of equilibrium, should there be one. It was found that a solution of phosphorous acid containing about 3.9 grams per liter and a solution of mercuric chloride containing about 26 grams per liter best served the purpose for preliminary experiments. Mercuric chloride is too difficultly soluble for more concentrated solutions. At temperatures below 25° the velocity of the reaction was too small to permit of accurate determination. At 25° and 30° the velocities could be very accurately measured. For example, 100 cc. of a solution of phosphorous acid were mixed with 100 cc. of a solution of mercuric chloride in a 500 cc. flask provided with an aspirator, and put in a thermostat at a temperature of 30°. At intervals of 5 and 10 hours, 10 cc. were drawn from the flask and titrated with a 0.05 N solution of sodium hydroxide, with methyl orange as indicator. In 545 hours, 16.2 cc. of sodium hydroxide were required to neutralize 10 cc. of the mixture; thus the reaction was practically complete in that time. This indicated that there was no equilibrium point.

For the accurate determinations, 500 cc. of each solution were mixed in a two-liter flask provided with an aspirator, and placed in the thermostat at the temperatures indicated in the tables. Fifty cc. were used for each titration. Methyl orange was the indicator used.

Theory and Formulae

Since it is obvious that in this reaction more than one substance changes concentration, we can therefore eliminate

the possibility of its being of the first order. Our supposition is that it is of the second, third, or fourth order. If it is of the second order, since we have used equivalent solutions, it must conform to the equation

$$\frac{dx}{dt} = K(a - x)^2 \qquad (I)$$

or

$$K = \frac{1}{t}\left(\frac{x}{a(a-x)}\right) \qquad (II)$$

If the reaction is of the third order, it would be expressed by the equation

$$\frac{dx}{dt} = K(a - x)^3 \qquad (III)$$

or

$$K = \frac{1}{2t}\left[\frac{1}{(a-x)^2} - \frac{1}{a^2}\right] \qquad (IV)$$

Finally, if it is of the fourth order, it would be expressed by the equation

$$\frac{dx}{dt} = K(a - x)^4 \qquad (V)$$

or

$$K = \frac{1}{3t}\left[\frac{1}{(a-x)^3} - \frac{1}{a^3}\right] \qquad (VI)$$

The calculations were made upon the following assumption: that the increase in acidity was dependent upon the concentration of the mercuric chloride solution. Hence, by taking the concentration of the mercuric chloride in 25 cc. and from the equation

$$2HgCl_2 = 2HCl$$
$$541.8 : \text{conc. of } HgCl_2 :: 72.9 : x,$$

the total increase can be found. Equating this with the hydroxide used in the titrations gives the value in cc. of the hydroxide. This number is then represented by (a) and the amount changed during any interval of time, equal to the increase in the amount of hydroxide required, is represented by (x).

The progress of the reaction was found by subtracting the number of cc. of hydroxide equivalent to 25 cc. of the phosphorous acid solution from the amount necessary to neutralize 50 cc. of the mixture at the time of titration. Substitutions were then made in equations II, IV, and VI, above.

Table I—(30° C.)

Mercuric chloride, 26.75 grams per liter
Phosphorous acid, 3.981 grams per liter

Time (hours)	a	$a-x$	x	$K^2 \times 10^4$	$K^3 \times 10^6$	$K^4 \times 10^9$
5	48.66	39.91	8.75	434	205	471
10	48.66	35.84	12.82	357	168	434
20	48.66	30.24	18.42	304	169	458
21	48.66	30.05	18.61	294	159	446
22	48.66	29.74	18.92	348	160	444
44	48.66	26.29	22.37	202	132	442
45	48.66	24.49	24.17	219	138	439
48	48.66	23.50	25.16	231	145	474
79	48.66	20.49	28.17	174	124	453
92	48.66	19.10	29.56	168	126	488
164	48.66	16.33	32.33	120	101	480
165	48.66	16.09	32.57	122	103	466

The 24.33 cc. of base used in titration are equivalent to the phosphorous acid contained in 50 cc. of the mixture.

Table II—(25° C.)

Mercuric chloride, 26.677 grams per liter
Phosphorous acid, 1.99 grams per liter

Time (hours)	a	$a-x$	x	$K^3 \times 10^6$	$K^4 \times 10^7$
5.33	29.56	23.57	5.99	41.09	13.53
20.0	29.56	19.92	9.64	34.39	14.63
127.5	29.56	12.07	17.49	22.43	13.85
228.0	29.56	19.53	20.03	19.28	13.92
491.0	29.56	8.00	21.56	14.78	13.67

The 14.78 cc. of base used in titration are equivalent to the phosphorous acid contained in 50 cc. of the mixture.

Table III—(25° C.)

Mercuric chloride, 26.4 grams per liter
Phosphorous acid, 0.9378 gram per liter

Time (hours)	a	$a-x$	x	$K^3 \times 10^6$	$K^4 \times 10^7$
5.2	13.2	7.61	5.59	11.084	11.758
20.0	13.2	5.19	7.91	7.846	11.197
179.0	13.2	2.22	10.98	5.507	16.939

The 6.60 cc. of base used in titration are equivalent to the phosphorous acid contained in 50 cc. of the mixture.

Table IV—(25° C.)

Mercuric chloride, 26.677 grams per liter
Phosphorous acid, 5.971 grams per liter

Time (hours)	a	$a-x$	x	$K^3 \times 10^6$	$K^4 \times 10^7$
38.9	61.32	42.26	19.06	37.76	7.60
90.0	61.32	35.08	26.24	30.3	6.97
181.8	61.32	28.27	33.05	27.0	7.32
248.0	61.32	25.71	35.61	25.1	7.32

The 42.40 cc. of base used in titration are equivalent to the phosphorous acid contained in 50 cc. of the mixture.

Table V—(30° C.)

Mercuric chloride, 20.01 grams per liter
Phosphorous acid, 3.693 grams per liter

Time (hours)	a	$a-x$	x	$K^3 \times 10^6$	$K^4 \times 10^7$
5.66	48.41	43.88	4.58	8.03	1.77
10.16	48.41	41.80	6.61	7.32	1.59
20.33	48.41	37.66	10.75	6.83	1.61
80.0	44.95	26.7	18.15	5.53	1.72
126.33	44.95	23.38	21.57	5.24	1.77
174.66	44.95	21.44	23.57	4.81	1.72
249.66	44.95	19.54	25.41	4.24	1.68
441.08	44.95	16.09	27.86	3.81	1.73

The 29.51 cc. of base used in titrations 1 to 3 are equivalent to the phosphorous acid in 50 cc. of the mixture.

The 27.42 cc. of base used in titrations 4 to 8 are equivalent to the phosphorous acid in 50 cc. of mixture.

Table VI—(30° C.)

Mercuric chloride, 13.33 grams per liter
Phosphorous acid, 3.693 grams per liter

Time (hours)	a	$a-x$	x	$K^3 \times 10^6$	$K^4 \times 10^7$
5.16	32.48	27.34	5.14	33.73	4.84
22.16	32.48	25.53	6.95	17.64	4.63
46.0	32.48	21.88	10.60	14.51	4.79
77.75	32.48	19.63	12.85	11.84	4.41
121.83	32.48	17.29	15.19	10.31	4.49
168.25	32.48	15.84	16.64	9.60	4.44
218.5	32.48	14.31	18.17	9.44	4.75

The 29.51 cc. of base used in titration are equivalent to the phosphorous acid in 50 cc. of the mixture.

Table VII—(30° C.)

Mercuric chloride, 6.669 grams per liter
Phosphorous acid, 3.693 grams per liter

Time (hours)	a	$a-x$	x	$K^3 \times 10^6$	$K^4 \times 10^7$
5.90	16.12	12.63	3.57	20.2	1.45
10.0	16.12	10.92	5.22	22.6	1.41
22.0	16.12	9.77	6.37	15.0	1.26
38.66	14.02	8.23	5.79	12.4	1.22
131.08	14.02	5.90	8.12	9.02	1.14
171.75	16.12	5.25	10.89	9.74	1.29
235.33	16.12	4.59	11.65	9.27	1.14

The 29.51 cc. of base used in titration are equivalent to the phosphorous acid contained in 50 cc. of the mixture.

Table VIII—(30° C.)

Mercuric chloride, 3.333 grams per liter
Phosphorous acid, 3.693 grams per liter

Time (hours)	a	$a-x$	x	$K^3 \times 10^6$	$K^4 \times 10^7$
5.0	8.07	6.61	1.35	76.0	10.57
9.9	8.07	5.76	2.31	73.79	11.2
21.75	8.07	4.85	3.21	61.52	10.5
77.3	8.07	3.31	4.76	44.08	10.96
237.0	8.07	2.18	6.89	43.25	10.5

The 29.51 cc. of base used in titration are equivalent to the phosphorous acid contained in 50 cc. of the mixture.

CONCLUSIONS

A careful examination of the results of this study of the interaction of mercuric chloride and phosphorous acid justifies, we believe, the following conclusions:

(1) That at temperatures of 25° and 30° and with the varied concentrations, the products of the reaction are mercurous chloride, orthophosphoric acid, and hydrochloric acid. No metallic mercury is deposited.

(2) That there is no equilibrium point, but the reaction goes to completion and the equation

$$2HgCl_2 + H_3PO_3 + H_2O \longrightarrow H_3PO_4 + 2HgCl + 2HCl$$

adequately expresses the facts.

(3) That since the values for the second and third order equations decrease rapidly, and those of the fourth order are reasonably constant, this reaction is obviously one of the fourth order. Therefore the velocity constant of the change is expressed by the equation

$$K = \frac{1}{3t}\left[\frac{1}{(a-x)^3} - \frac{1}{a^3}\right].$$

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THE CONDUCTIVITY, TEMPERATURE COEFFICIENTS OF CONDUCTIVITY AND DISSOCIATION OF CERTAIN ELECTROLYTES IN AQUEOUS SOLUTION FROM 0° TO 35°. PROBABLE INDUCTIVE ACTION IN SOLUTION, AND EVIDENCE FOR THE COMPLEXITY OF THE ION

BY L. G. WINSTON AND HARRY C. JONES

INTRODUCTION

This paper forms one of a series dealing with the conductivity of electrolytes in aqueous solution. In it we shall take

up for consideration the conductivity, temperature coefficients of conductivity, and percentage dissociation of certain salts, and shall show how these results confirm those already obtained, and point out some new relations. The work is part of an investigation which has been carried on in this laboratory for a dozen years or more. The importance of such an investigation is obvious, since chemistry is a branch of the science of solutions, and one of the very best methods of studying solutions is the conductivity method.

HISTORICAL

Electrochemical theories were advanced as early as 1807 by Davy and by Berzelius. Berzelius was among the first to call attention to the electrically charged atom. Faraday appeared later, giving to the world the laws which bear his name. His work has stood the test of time. His law showing the relation between the quantity of electricity and amount of decomposition holds rigidly to-day, and in the light of the electron theory takes on a new meaning. In the years 1853 to 1859 Hittorf determined the relative velocities of the ions of many salts. He pointed out a relation between chemical activity and conductivity, and also called attention to the analogy existing between solutions and gases. This latter problem was taken up later by Raoult, Ostwald, van't Hoff, and others. The laws of Raoult, dealing with the lowering of the freezing point and vapor pressure of liquids, and Ostwald's dilution law are well known. Van't Hoff, in 1887, working on osmotic pressure, found certain solutions that behaved abnormally. Arrhenius, attempting to explain their behavior, pointed out the fact that salts and analogous substances break down into ions. Thus was given to the world the theory of electrolytic dissociation. Its truth is attested on every hand. Facts once inexplicable become wonderfully clear and lend confirmation to the theory. Many workers have appeared in the field since Arrhenius. The most important of these, perhaps, is Sir J. J. Thomson, whose brilliant experiments have well-nigh revolutionized our conception of matter.

The result of the work already done may be summarized briefly as follows: The conductivity of electrolytes in solution is dependent primarily on two things, viz., the number of ions and their velocity. These two factors may be affected by various others. The most important of these is temperature. The effect of rise in temperature is chiefly to increase the velocity of the ions. The number of ions would not be greatly affected unless they were complex. In addition to the effect of temperature on the number and velocity of ions in solution, there are still other factors which, for convenience, may be divided into three classes:

1. Those dependent upon the solute.
2. Those dependent upon the solvent.
3. Those dependent upon the combination of the solvent with the solute.

In class 1—factors dependent upon the solute—mention should be made first of all of the effect of valence. This would determine largely the number of ions capable of entering into solution. As is well known, the conductivities of binary, ternary and quaternary compounds are found to vary considerably. Factors affecting the velocity of the ion would be the atomic weights and atomic volumes of the elements existing in the compound. We would naturally expect that the velocity would be an inverse function of the atomic weight and atomic volume. Experimentally, however, this has not been found to be true. Jones and Pearce[1] found that those elements which have the smallest atomic volumes have the greatest hydrating power. This would tend to diminish their velocity.

As to the factors dependent upon the solvent, the most important are its viscosity, its dielectric constant and its association.

In class 3 should be placed the concentration of the solution and the power of the solute and solvent to form solvates with one another.

The conductivity of solutions has been studied from each of

[1] THIS JOURNAL, **38**, 737 (1907).

these standpoints, and much valuable data have been accumulated.

The effect of temperature has been worked out carefully by Jones and his coworkers, West,[1] Jacobson,[2] Clover,[3] West,[4] White,[5] Wightman,[6] and Hosford.[7] Conductivity always increases with rise in temperature from 0° to 65°, while dissociation usually decreases slightly. The decrease in dissociation would tend to diminish the number of ions, and thus to lessen the conductivity, but this effect is more than offset by the increased velocity of the ions due to rise in temperature. This decrease in dissociation may be accounted for in two ways. It may be due to a decrease in the association of the solvent, which would tend to decrease the dissociation of the dissolved substance; or it may be due to the fact that a rise in temperature diminishes the dielectric constant of the solvent and consequently its dissociating power, since, according to the Thompson-Nernst hypothesis, a substance having a high dielectric constant has great dissociating power. While, as just shown, the effect of temperature is to diminish the number of ions present, its effect on the velocity of ions is just the reverse. Rise in temperature increases the velocity of ions in two ways: First, it diminishes the viscosity of the solvent. Second, rise in temperature would decrease the complexity of the hydrates formed. This also would tend to increase the velocity of the ions. At all events, the decrease in the number of ions seems to be more than compensated for by the increase in their velocity, and the general effect of rise in temperature is, therefore, to increase the conductivity.

The most important factor in its effect on conductivity with rise in temperature is hydration. That the dissolved substance combines with some of the solvent to form solvates seems now to be an undisputed fact, the existence of hydrates

[1] THIS JOURNAL, **34**, 357 (1905).
[2] *Ibid.*, **40**, 355 (1908).
[3] *Ibid.*, **43**, 187 (1910).
[4] *Ibid.*, **44**, 508 (1910).
[5] *Ibid.*, **44**, 159 (1910).
[6] *Ibid.*, **46**, 56 (1911).
[7] *Ibid.*, **46**, 240 (1911).

in solution being shown by several independent lines of evidence.[1] The close connection between hydration and water of crystallization has also been established in this laboratory.

Important relations between amount of hydration and temperature coefficients of conductivity have been pointed out. Jones and his coworkers, Bingham, McMaster, Rouiller,[2] Veazey,[3] Guy,[4] Davis, Reinhart, Mahin,[5] Schmidt,[6] and Kreider[7] have made important observations on the effect of viscosity on the conductivity of electrolytes.

The work in this laboratory has been extended to non-aqueous solutions. Apparatus has been improved, the range of temperature has been extended, old sources of error have been eliminated, and the conductivities of hundreds of compounds have been added to those already measured.

The problem has been undertaken in this laboratory of *measuring the conductivity of all of the more common acids, bases and salts in aqueous solution, from 0° to 65°*, and of calculating the dissociation whenever possible.

This work will be pushed forward as rapidly and carefully as possible.

One fact, overlooked thus far in the consideration of the conductivity of electrolytes, is the probable inductive action[8] of the ion on the unionized molecule. In the solution of a salt there is every condition necessary for inductive action. There are the charged ions, the neutral molecules and the dielectric or solvent. Ordinary electrical induction in conductors, as is well known, takes place as follows: A charged body brought near to a neutral body, but separated from it by a dielectric, causes a separation of the electricity in the neutral body, drawing the opposite kind nearest to itself and repelling the like charge to the side farthest from itself. If, while the charged body is still near, the repelled charge in the

[1] Publication No. **60** of the Carnegie Institution of Washington.
[2] Publication No. **80** of the Carnegie Institution of Washington.
[3] THIS JOURNAL, **41**, 433 (1909).
[4] *Ibid.*, **46**, 131 (1911).
[5] *Ibid.*, **41**, 433 (1909).
[6] *Ibid.*, **42**, 37 (1909).
[7] *Ibid.*, **45**, 282 (1911).
[8] See paper in THIS JOURNAL (**45**, 547, (1911)) by L. G. Winston, to whom this entire suggestion and its applications in this and the preceding paper are due.

conductor is removed by contact with some other body, on the removal of the charged body the once neutral body would be left charged with the opposite kind of electricity. The ion, a charged body, acting through the water (a dielectric) on an unionized molecule, would produce just such an effect. Several results may follow from this. First, a positive ion brought near to a neutral molecule, but separated from it by the nonconducting water, would cause a separation of the electricity in the molecule; the negative will be drawn near to the ion and the positive repelled. Suppose, for instance, that the repelled charge is not removed, the charged ion would simply attach itself to the molecule, and as a charged system move through the solution. Moreover, this charged system could play the part of the original ion and, acting through the water, in a similar way draw other molecules to itself. There would be a limit, of course, to the number of molecules which could thus be attached. This, no doubt, would be a function of the valency of the ion.

If, on the other hand, the repelled charge is removed and the inducing ion then moves off, the once neutral molecule would be left charged with a sign opposite to that on the inducing ion, and moving through the solution would be able to attract other molecules or oppositely charged ions to itself. This, of course, would give rise to a great complexity of ions and molecules. The velocity of the ions would thus be greatly affected, because their masses would be greatly increased. This may in a measure account for the apparent discrepancy between the dissociation as found by the freezing point method and that found by conductivity, since by this inductive action there would be brought about a change in the number of particles which would probably affect the dissociation as found by the freezing point method.

The effect on conductivity, on the other hand, would be due rather to a change in the velocity of the ions. The complex ions would tend to move more slowly than the individual ion, thus making the conductivity measurements of dissociation too low. The change in the number of particles would not be so apparent in the case of conductivity because, when,

by means of induction, an ion attaches itself to a neutral molecule, it would still give rise to a charged system, and would not thereby reduce the number of charged particles in solution. The breaking up of these moving systems by heat would show itself in increased temperature coefficients.

Jones and Pearce[1] have shown that the dissociation as measured by the conductivity method is less than that calculated from the freezing point lowering. Conditions were chosen such that the number of ions, velocity of ions, hydration and viscosity were the same in both cases. It was found by them that the greater the dilution, the greater the difference in dissociation as measured by the two methods. This is due to the fact that the complexity of the hydrate is greater, the greater the dilution.

Evidence seems to be accumulating in many directions that the ions in solution are complex. Some interesting relations are brought out in connection with the various dilution laws, to which sufficient attention has not as yet been directed, which apparently point to the complexity of molecules in solution. Ostwald's law,

$$\frac{\alpha^2}{(1-\alpha)V} = K$$

has been found to apply to weakly dissociated electrolytes, but not at all to strong electrolytes. Moreover, various dilution laws have been formulated which apply to strong electrolytes but are extremely unsatisfactory when it is attempted to apply them to weaker electrolytes.

The question naturally arises, why this difference? The thought has suggested itself that it may be due to the complexity of the molecule—one dilution law applying to solutions containing molecules of a certain complexity, while another would apply to solutions containing molecules of a different order of complexity. Of the many dilution laws for strong electrolytes only two will be considered, viz., that of Rudolphi and that of van't Hoff. The Rudolphi formula is

[1] THIS JOURNAL, **38**, 743 (1907).

$$\frac{\alpha^2}{(1-\alpha)\sqrt{V}} = K$$

Van't Hoff's is

$$\frac{\alpha^3}{(1-\alpha)^3 V} = K$$

Since the Ostwald law,

$$\frac{\alpha^2}{(1-\alpha)V} = K$$

applies to weakly dissociated electrolytes, in solutions to which it applies there are very few ions. If the Rudolphi formula is applied to a solution, a certain volume, V_1, is obtained, corresponding to a definite value for α and for K. If now, retaining the same values as before for α and for K, the Ostwald formula is applied to the same solution, there is obtained a volume V which is the square root of the volume obtained by the Rudolphi formula. In other words, there is found the relation $\sqrt{V_1}/V = 1$, a relation which would indicate complexity of the molecule in solutions to which the Rudolphi formula applies. Treating the van't Hoff formula in the same way, i. e., comparing the volume obtained by the use of the van't Hoff formula with a certain solution, for a definite value of α and of K, with the volume obtained by the use of the Ostwald formula for the same solution, keeping α and K the same as before, there is found the relation

$$\frac{V}{V_1} = \frac{\alpha}{1-\alpha}$$

where V represents the volume when the Ostwald law was applied and V_1 the volume obtained when the van't Hoff law was used. Now if $V/V_1 = constant$, the molecule would be simple in each case; but on examining the formula it is readily seen that the relation is not a constant one, but that it is a function of the dissociation. This would indicate complexity of the molecule in solutions to which the van't Hoff law applies. The interesting fact about this last relation is that the degree of complexity varies with the dissociation, i. e., with the number of ions present; just exactly what has been referred to above as

the probable result of inductive action. Let us now turn to the consideration of the data in hand.[1]

EXPERIMENTAL

The well known Kohlrausch method was used to determine the conductivities. A Kohlrausch slide wire bridge was employed with an induction coil and telephone receiver. The cells used were of the type designed by Jones and Bingham.[2] The cell constants were redetermined at regular, short intervals. The measurements were made at 0°, 12°.5, 25°, and 35°. Three separate readings were taken for each solution at each temperature, different resistances being used for each reading. The average of the conductivities obtained by using each of these readings was taken to be the correct conductivity.

The flasks and burettes were carefully calibrated at 20° by the method of Morse and Blalock.[3]

Solutions

Kahlbaum's "chemically pure" materials were taken as the starting point in almost every case. These were purified, whenever practicable, by crystallization. A solution somewhat more concentrated than the most concentrated solution to be used was made up. Its strength was determined by volumetric or gravimetric methods, and the solutions prepared from it as a mother solution. This solution was made by direct weighing whenever it was possible, and in the measurements given below this method was always used unless otherwise stated.

Water

The water used in making the solutions was prepared according to the method of Jones and Mackay,[4] which has been employed in this laboratory for many years. This method is

[1] It should be stated that all of the above relations have been worked out entirely independently by L. G. Winston.

[2] THIS JOURNAL, **34**, 493 (1903).

[3] *Ibid.*, **18**, 479 (1894).

[4] *Ibid.*, **19**, 91 (1897).

too well known to need discussion here. The water thus obtained had a conductivity of about 0.9 to 1.3×10^{-6} at 0°.

Discussion of Results

The following salts have been classified, approximately, according to the position of the metal in the Periodic System. The ammonium, potassium and sodium compounds would, therefore, be first in order. These are, therefore, grouped together for consideration. A careful examination of the results for these compounds will show some points of interest.

(1) The difference in the conductivities of the binary, ternary and quaternary salts is quite evident. The conductivity of ammonium nitrate, potassium acetate, and potassium permanganate, between 0° and 35°, ranges from 46 at 0°, in the most concentrated solution of potassium acetate, to 163.62 at 35° in the most dilute solution of ammonium nitrate. The conductivity of those compounds which are not binary, viz., ammonium sulphate, acid ammonium sulphate, dipotassium phosphate, sodium sulphate, and borax, at 35° in the most dilute solutions is, in every case, above 200, and for acid ammonium sulphate is considerably above 500.

The very high values for the temperature coefficients of conductivity, expressed in conductivity units, in the case of the four sulphates is very noticeable. The highest values are 5, 6, and 7+ in the case of sodium sulphate, ammonium sulphate and acid ammonium sulphate, respectively; while for the other salts under consideration in this group, the temperature coefficients in conductivity units is 4+. This is probably due to the fact that sulphates show a tendency towards polymerization.

The very largest temperature coefficient of conductivity of this group belongs to acid ammonium sulphate. It is 7.96. This is doubtless accounted for by the fact that this salt breaks up into very complex ions.

In the case of potassium acetate and potassium permanganate, it is somewhat peculiar that the temperature coefficients of conductivity in per cent. are in both cases, from 0°

through 25°, larger than those measured in conductivity units.

It is also striking that in the case of acid ammonium sulphate the temperature coefficients of conductivity decrease with rise in temperature.

In dealing with the following data the percentage dissociation is not discussed for the individual salts, but by means of curves which are given after the data their points of difference are brought out.

Ammonium Nitrate

Table I—Conductivity

V	0°	12°.5	25°	35°
2	58.44	78.92	101.51	119.48
8	64.35	84.25	113.38	135.07
32	68.81	94.30	123.13	146.53
128	71.64	98.45	128.44	152.92
512	73.63	101.39	132.64	157.48
1024	74.69	102.51	134.43	159.44
2048	75.25	103.39	134.79	160.39
4096	76.37	105.51	137.87	163.62

Table II—Temperature Coefficients

	0°–12°.5		12°.5–25°		25°–35°	
V	Cond. units	Per cent.	Cond. units	Per cent.	Cond. units	Per cent.
2	1.64	2.81	1.81	2.29	1.80	1.77
8	1.59	2.47	2.33	2.77	2.17	1.91
32	2.04	2.97	2.31	2.45	2.34	1.90
128	2.15	3.00	2.40	2.44	2.45	1.91
512	2.22	3.02	2.50	2.47	2.48	1.86
1024	2.23	2.99	2.55	2.49	2.50	1.86
2048	2.25	2.99	2.52	2.44	2.56	1.90
4096	2.33	3.05	2.59	2.46	2.58	1.87

Table III—Percentage Dissociation

V	0°	12°.5	25°	35°
2	76.5	74.8	73.6	73.0
8	84.2	79.9	82.2	82.6
32	90.1	89.4	89.3	90.0
128	93.8	93.3	93.2	93.5
512	96.4	96.1	96.2	96.3
1024	97.8	97.2	97.5	97.5
2048	98.5	98.0	97.8	98.0
4096	100.0	100.0	100.0	100.0

Ammonium Sulphate

Table IV—Conductivity

V	0°	12°.5	25°	35°
2	82.37	112.09	145.09	170.72
8	98.06	136.28	179.57	213.19
32	115.27	160.26	210.98	254.86
128	130.95	182.65	241.38	291.69
512	139.69	195.77	259.21	313.00
1024	143.84	202.31	267.62	322.55
2048	150.62	209.74	275.96	337.47
4096	150.44	211.55	280.82	340.32

Table V—Temperature Coefficients

	0°–12°.5		12°.5–25°		25°–35°	
V	Cond. units	Per cent.	Cond. units	Per cent.	Cond. units	Per cent.
2	2.38	2.89	2.64	2.36	2.56	1.76
8	3.06	3.12	3.46	2.54	3.36	1.87
32	3.60	3.12	4.06	2.53	4.39	2.08
128	4.14	3.16	4.70	2.57	5.03	2.08
512	4.49	3.21	5.08	2.60	5.38	2.08
1024	4.68	3.25	5.22	2.58	5.49	2.05
2048	4.73	3.14	5.30	2.53	6.15	2.23
4096	4.89	3.25	5.54	2.58	5.95	2.12

Table VI—Percentage Dissociation

V	0°	12°.5	25°	35°
2	54.6	52.9	51.6	50.1
8	65.0	64.4	63.9	62.6
32	76.5	75.7	75.1	74.8
128	86.9	86.3	85.9	85.7
512	92.7	92.5	92.3	91.9
1024	95.4	95.6	95.2	94.7
2048	100.0	99.1	98.2	99.1
4096	99.8	100.0	100.0	100.0

Acid Ammonium Sulphate

Table VII—Conductivity

V	0°	12°.5	25°	35°
2	155.26	186.49	211.99	226.06
8	183.40	223.84	258.00	277.18
32	223.58	279.55	322.68	349.24
128	265.24	339.00	404.14	444.74
512	289.79	378.25	463.20	522.24
1024	295.22	386.88	483.51	547.05
2048	303.41	400.01	496.86	573.46
4096	304.26	401.96	497.11	576.66

Table VIII—Temperature Coefficients

	0°–12°.5		12°.5–25°		25°–35°	
V	Cond. units	Per cent.	Cond. units	Per cent.	Cond. units.	Per cent.
2	2.50	1.61	2.04	1.09	1.41	0.66
8	4.04	2.20	2.73	1.22	1.91	0.74
32	4.48	2.00	3.45	1.23	2.66	0.82
128	5.90	2.22	5.21	1.54	4.06	1.01
512	7.08	2.44	6.79	1.80	5.90	1.27
1024	7.33	2.48	7.73	2.00	6.35	1.31
2048	7.73	2.55	7.74	1.94	7.66	1.54
4096	7.81	2.57	7.61	1.89	7.96	1.60

Table IX—Percentage Dissociation

V	0°	12°.5	25°	35°
2	51.0	46.4	42.7	39.2
8	60.3	55.7	51.9	48.1
32	73.5	69.6	65.0	60.6
128	87.1	84.4	81.3	77.1
512	95.2	94.2	93.2	90.5
1024	97.0	96.3	97.4	94.9
2048	99.7	99.6	99.9	99.4
4096	100.0	100.0	100.0	100.0

Sodium Sulphate

Table X—Conductivity

V	0°	12°.5	25°	35°
4	68.49	97.54	129.13	156.71
8	78.51	111.46	146.40	178.24
32	94.51	132.72	176.76	215.19
128	107.54	152.49	203.10	247.02
512	117.46	166.24	221.21	269.50
1024	119.65	169.61	226.34	276.92
2048	125.95	176.08	235.35	287.02
4096	127.73	181.61	243.42	294.48

Table XI—Temperature Coefficients

	0°–12°.5		12°.5–25°		25°–35°	
V	Cond. units	Per cent.	Cond. units	Per cent.	Cond. units	Per cent.
4	2.32	3.39	2.53	2.59	2.76	2.14
8	2.63	3.35	2.80	2.51	3.18	2.17
32	3.05	3.23	3.52	2.65	3.84	2.17
128	3.59	3.34	4.05	2.66	4.39	2.16
512	3.90	3.32	4.40	2.65	4.83	2.18
1024	4.00	3.34	4.54	2.68	5.06	2.19
2048	4.01	3.18	4.74	2.69	5.17	2.20
4096	4.31	3.37	4.94	2.72	5.11	2.10

Table XII—Percentage Dissociation

V	0°	12°.5	25°	35°
4	53.6	53.7	53.1	53.2
8	61.4	61.4	60.1	60.5
32	73.9	73.1	72.6	73.0
128	84.1	84.0	83.4	83.9
512	91.9	91.6	90.9	91.5
1024	93.6	93.4	93.0	94.0
2048	98.5	97.0	96.7	97.4
4096	100.0	100.0	100.0	100.0

Borax

Table XIII—Conductivity

V	0°	12°.5	25°	35°
16	57.99	83.76	113.54	139.83
32	64.36	92.74	125.49	154.61
128	72.87	104.81	141.72	174.52
512	78.04	112.22	152.00	187.97
1024	79.20	113.29	153.40	189.37
2048	83.45	119.55	161.23	198.31
4096	85.50	122.28	163.99	202.65

Table XIV—Temperature Coefficients

	0°–12°.5		12°.5–25°		25°–35°	
V	Cond. units	Per cent.	Cond. units	Per cent.	Cond. units	Per cent.
16	2.06	3.55	2.38	2.84	2.63	2.32
32	2.27	3.53	2.62	2.83	2.91	2.32
128	2.56	3.51	2.95	2.82	3.28	2.32
512	2.73	3.50	3.18	2.83	3.60	2.37
1024	2.73	3.45	3.21	2.83	3.60	2.35
2048	2.89	3.46	3.33	2.79	3.71	2.30
4096	2.94	3.44	3.34	2.73	3.87	2.36

Table XV—Percentage Dissociation

V	0°	12°.5	25°	35°
16	67.8	68.5	69.2	69.0
32	75.3	75.8	76.5	76.3
128	85.3	85.7	86.4	86.1
512	91.3	91.8	92.7	92.7
1024	92.7	92.6	93.5	93.4
2048	97.6	97.8	98.3	97.8
4096	100.0	100.0	100.0	100.0

Potassium Acetate

Table XVI—Conductivity

V	0°	12°.5	25°	35°
4	46.13	62.62	83.35	99.88
8	48.60	67.11	88.43	105.87
32	53.09	73.59	97.29	117.46
128	55.57	77.43	102.13	123.03
512	57.17	79.91	105.16	126.87
1024	58.33	81.14	106.84	129.09
2048	59.24	82.09	108.43	129.84
4096	59.06	81.89	108.65	129.90

Table XVII—Temperature Coefficients

	0°–12°.5		12°.5–25°		25°–35°	
V	Cond. units	Per cent.	Cond. units	Per cent.	Cond. units	Per cent.
4	1.32	2.86	1.66	2.64	1.65	1.98
8	1.48	3.05	1.71	2.55	1.74	1.97
32	1.64	3.09	1.90	2.58	2.02	2.07
128	1.75	3.15	1.98	2.54	2.09	2.05
512	1.82	3.17	2.02	2.53	2.17	2.06
1024	1.83	3.14	2.06	2.54	2.23	2.09
2048	1.83	3.09	2.11	2.57	2.14	1.97
4096	1.83	3.10	2.14	2.61	2.13	1.96

Table XVIII—Percentage Dissociation

V	0°	12°.5	25°	35°
4	77.8	76.3	76.6	76.9
8	82.0	81.8	81.3	81.5
32	89.6	89.7	89.5	90.4
128	93.7	94.4	93.9	94.7
512	96.4	97.4	96.7	97.6
1024	98.4	98.9	98.3	99.3
2048	100.0	100.0	99.7	99.9
4096	99.6	99.8	100.0	100.0

Potassium Permanganate

The strength of the mother solution was determined volumetrically by means of potassium tetroxalate.

Table XIX—Conductivity

V	0°	12°.5	25°	35°
8	59.34	80.17	104.36	124.74
32	63.75	87.13	113.70	136.05
128	66.76	91.38	119.31	142.42
512	66.46	91.14	117.90	141.49
1024	64.65	89.05	113.95	137.09
2048	63.72	86.61	110.80	133.02
4096	62.64	87.94	111.80	133.97

Table XX—Temperature Coefficients

	0°–12°.5		12°.5–25°		25°–35°	
V	Cond. units	Per cent.	Cond. units	Per cent.	Cond. units	Per cent.
8	1.67	2.81	1.94	2.42	2.04	1.96
32	1.87	2.93	2.13	2.45	2.24	1.97
128	1.97	2.95	2.23	2.44	2.31	1.94
512	1.97	2.96	2.14	2.35	2.36	2.00
1024	1.95	3.02	1.99	2.24	2.31	2.03
2048	1.83	2.87	1.94	2.24	2.22	2.00
4096	2.02	3.23	1.91	2.17	2.22	1.99

Table XXI—Percentage Dissociation

V	0°	12°.5	25°	35°
8	88.8	87.7	87.5	87.6
32	95.4	95.3	95.3	95.5
128	100.0	100.0	100.0	100.0
512	99.5	99.7	98.8	99.4
1024	96.8	97.4	95.5	96.3
2048	95.4	94.8	92.9	93.4
4096	93.8	96.2	93.7	94.1

Dipotassium Phosphate

This salt was precipitated by magnesia mixture and the phosphoric acid thus determined.

Table XXII—Conductivity

V	0°	12°.5	25°	35°
2	63.01	86.82	113.04	138.16
8	79.19	109.25	143.34	174.91
32	91.69	127.42	167.61	203.80
128	102.47	142.37	188.10	230.71
512	107.76	150.85	199.40	239.84
1024	109.35	152.23	200.52	242.65
2048	110.47	157.04	206.13	242.54
4096	107.16	154.98	201.98	250.78

Table XXIII—Temperature Coefficients

	0°–12°.5		12°.5–25°		25°–35°	
V	Cond. units	Per cent.	Cond. units	Per cent.	Cond. units	Per cent.
2	1.91	3.03	2.10	2.42	2.51	2.22
8	2.40	3.03	2.73	2.50	3.16	2.21
32	2.86	3.05	3.22	2.53	3.62	2.16
128	3.19	3.11	3.66	2.57	4.26	2.27
512	3.45	3.20	3.88	2.57	4.04	2.03
1024	3.43	3.14	3.86	2.54	4.21	2.10
2048	3.73	3.38	3.93	2.50	3.64	1.77
4096	3.83	3.57	3.76	2.43	4.88	2.42

Table XXIV—Percentage Dissociation

V	0°	12°.5	25°	35°
2	57.0	55.3	54.8	55.1
8	71.7	69.6	69.5	69.8
32	83.0	81.1	81.3	81.3
128	92.8	90.7	91.3	92.0
512	97.6	96.1	96.7	95.7
1024	99.0	96.9	97.3	96.8
2048	100.0	100.0	100.0	96.7
4096	97.0	98.7	98.0	100.0

The group consisting of strontium acetate and magnesium bromide, nitrate, formate and acetate will be considered next.

There is nothing special to note in the case of strontium acetate. It is readily hydrolyzed, and any irregularities might easily be attributed to this fact. Attention might be called, however, to the increase in percentage dissociation with rise in temperature.

It is interesting in considering the data of the four magnesium compounds to discover, if possible, the effect of the different anions. Of course, the water of crystallization would also be a factor. This is the same, however, in the case of the bromide and nitrate, and any difference in the conductivity of these two compounds may correctly be attributed to the different anions.

On examining the data for these substances, it is readily seen that the conductivity of magnesium bromide is decidedly greater than that of magnesium nitrate. Its temperature coefficient of conductivity is also larger. This would point

to some difference in the anions either as to velocity or complexity. Apart from their remarkable similarity, magnesium acetate and formate present nothing of special interest.

Strontium Acetate

The strontium was precipitated and weighed as the carbonate.

Table XXV—Conductivity

V	0°	12°.5	25°	35°
2	34.94	49.26	66.52	81.11
8	56.51	80.19	106.96	129.99
32	70.69	100.20	135.25	164.88
128	81.89	117.19	157.69	193.44
512	88.50	128.09	170.16	209.22
1024	91.18	131.09	177.44	218.24
2048	97.30	139.01	180.07	219.77
4096	97.89	139.60	184.44	224.75

Table XXVI—Temperature Coefficients

	0°–12°.5		12°.5–25°		25°–35°	
V	Cond. units	Per cent.	Cond. units	Per cent.	Cond. units	Per cent.
2	1.15	3.29	1.38	2.80	1.46	2.20
8	1.89	3.35	2.14	2.67	2.30	2.15
32	2.36	3.34	2.80	2.79	2.96	2.19
128	2.82	3.44	3.24	2.77	3.58	2.27
512	3.17	3.58	3.37	2.63	3.91	2.30
1024	3.19	3.50	3.70	2.82	4.08	2.30
2048	3.34	3.43	3.28	2.36	3.97	2.21
4096	3.34	3.41	3.59	2.57	4.03	2.19

Table XXVII—Percentage Dissociation

V	0°	12°.5	25°	35°
2	35.7	35.3	36.1	36.1
8	57.7	57.4	58.0	57.8
32	72.2	71.8	73.4	73.4
128	83.6	83.9	85.5	86.1
512	90.4	91.7	92.3	93.1
1024	93.1	93.9	96.4	97.1
2048	99.3	99.6	97.7	97.8
4096	100.0	100.0	100.0	100.0

Magnesium Bromide

The magnesium was prcipitated as ammonium magnesium phosphate, and weighed as the pyrophosphate.

Table XXVIII—Conductivity

V	0°	12°.5	25°	35°
2	76.34	104.05	132.92	162.25
8	93.73	130.12	170.64	206.18
32	104.56	147.24	194.42	235.51
128	113.52	159.94	211.91	257.31
512	118.93	167.72	223.06	270.40
1024	122.80	173.39	230.94	279.38
2048	127.28	179.74	238.70	289.52
4096	130.91	185.06	244.94	305.94

Table XXIX—Temperature Coefficients

	0°–12°.5		12°.5–25°		25°–35°	
V	Cond. units	Per cent.	Cond. units	Per cent.	Cond. units	Per cent.
2	2.22	2.91	2.31	2.22	2.93	2.20
8	2.91	3.11	3.24	2.49	3.55	2.08
32	3.41	3.26	3.77	2.56	4.11	2.11
128	3.71	3.27	4.16	2.60	4.54	2.14
512	3.90	3.28	4.43	2.64	4.73	2.12
1024	4.05	3.30	4.60	2.65	4.84	2.10
2048	4.20	3.30	4.72	2.63	5.08	2.13
4096	4.33	3.31	4.79	2.59	6.10	2.49

Table XXX—Percentage Dissociation

V	0°	12°.5	25°	35°
2	58.3	56.2	54.3	53.0
8	71.6	70.3	69.7	67.4
32	79.9	79.5	79.4	76.9
128	86.8	86.4	86.5	84.1
512	90.9	90.6	91.1	88.3
1024	93.9	93.7	94.3	91.3
2048	97.3	97.1	97.5	94.6
4096	100.0	100.0	100.0	100.0

Magnesium Nitrate

The magnesium was weighed as the pyrophosphate.

Table XXXI—Conductivity

V	0°	12°.5	25°	35°
8	88.91	123.42	160.86	191.88
32	101.55	141.97	187.10	223.24
128	110.78	155.50	204.72	247.66
512	119.01	165.77	220.89	265.33
1024	120.68	170.27	224.49	272.30
2048	123.34	173.18	229.70	280.09
4096	122.89	173.70	229.58	277.54

Table XXXII—Temperature Coefficients

	0°–12°.5		12°.5–25°		25°–35°	
V	Cond. units	Per cent.	Cond. units	Per cent.	Cond. units	Per cent.
8	2.76	3.10	2.99	2.42	3.10	1.93
32	3.23	3.18	3.61	2.54	3.61	1.93
128	3.58	3.23	3.54	2.28	4.29	2.10
512	3.74	3.14	4.41	2.66	4.44	2.01
1024	3.97	3.28	4.34	2.55	4.78	2.12
2048	3.99	3.23	4.52	2.61	5.04	2.11
4096	4.06	3.30	4.47	2.57	4.80	2.09

Table XXXIII—Percentage Dissociation

V	0°	12°.5	25°	35°
8	72.1	71.1	70.0	68.5
32	82.4	81.7	81.5	79.7
128	89.9	89.5	89.1	88.4
512	96.5	95.4	96.2	94.7
1024	97.9	98.0	99.7	97.2
2048	100.0	99.7	100.0	100.0
4096	99.7	100.0	99.96	99.1

Magnesium Formate

The magnesium was weighed as the pyrophosphate.

Table XXXIV—Conductivity

V	0°	12°.5	25°	35°
2	37.33	52.53	69.24	83.25
8	58.15	83.44	109.29	132.14
32	74.68	106.05	141.71	172.31
128	85.99	122.17	164.06	200.30
512	88.58	123.84	167.86	205.44
1024	94.03	133.87	176.23	209.90
2048	97.22	138.60	184.73	226.37
4096	97.18	138.74	182.91	223.19

Table XXXV—Temperature Coefficients

	0°–12°.5		12°.5–25°		25°–35°	
V	Cond. units	Per cent.	Cond. units	Per cent.	Cond. units	Per cent.
2	1.22	3.27	1.33	2.53	1.40	2.02
8	2.02	3.47	2.07	2.48	2.29	2.10
32	2.51	3.36	2.85	2.69	3.06	2.16
128	2.89	3.36	3.35	2.74	3.62	2.21
512	2.82	3.18	3.52	2.84	3.76	2.24
1024	3.19	3.39	3.38	2.52	3.37	1.91
2048	3.31	3.40	3.69	2.66	4.16	2.25
4096	3.32	3.42	3.53	2.54	4.03	2.20

Table XXXVI—Percentage Dissociation

V	0°	12°.5	25°	35°
2	38.4	37.9	37.5	36.8
8	59.8	60.1	59.2	58.4
32	76.8	76.4	76.7	76.1
128	88.4	88.1	88.8	88.5
512	91.1	89.3	90.9	90.7
1024	96.7	96.5	95.4	92.7
2048	99.9	99.9	100.0	100.0
4096	100.0	100.0	99.05	98.6

Magnesium Acetate

The magnesium was determined as in the preceding salt.

Table XXXVII—Conductivity

V	0°	12°.5	25°	35°
4	37.56	54.50	72.50	88.92
8	46.35	66.76	89.79	109.86
32	60.99	87.97	119.31	146.20
128	71.13	103.35	139.51	172.35
512	78.05	113.23	153.41	189.50
1024	80.38	116.73	158.95	201.71
2048	83.85	121.36	164.72	203.07
4096	84.99	121.76	165.38	203.70

Table XXXVIII—Temperature Coefficients

	0°–12°.5		12°.5–25°		25°–35°	
V	Cond. units	Per cent.	Cond. units	Per cent.	Cond. units	Per cent.
4	1.36	3.62	1.44	2.64	1.64	2.26
8	1.63	3.52	1.84	2.76	2.01	2.24
32	2.16	3.54	2.51	2.85	2.69	2.25
128	2.58	3.63	2.89	2.80	3.28	2.35
512	2.81	3.60	3.21	2.83	3.61	2.35
1024	2.91	3.62	3.38	2.89	4.28	2.69
2048	3.00	3.58	3.47	2.86	3.84	2.33
4096	2.94	3.46	3.49	2.87	3.83	2.32

Table XXXIX—Percentage Dissociation

V	0°	12°.5	25°	35°
4	44.2	44.8	43.8	43.7
8	54.6	54.8	54.3	53.9
32	71.8	72.2	72.1	71.8
128	83.7	84.9	84.3	84.6
512	91.9	93.0	92.8	93.0
1024	94.6	95.9	96.1	99.0
2048	98.7	99.7	99.6	99.7
4096	100.0	100.0	100.0	100.0

The next group taken up for study consists of cadmium chloride, cadmium bromide, cadmium iodide and lead chloride. Attention should be called to the fact that cadmium iodide, having no water of crystallization, has just about the same temperature coefficients of conductivity as cadmium bromide and cadmium chloride, both of which have water of crystallization. Apparent increase of percentage dissociation with rise in temperature is unusual, and is quite noticeable in the case of cadmium iodide.

Lead chloride has no water of crystallization but, like cadmium iodide, has high temperature coefficients of conductivity. There must be some factor operative here affecting temperature coefficients just as hydration does, but which, from the nature of the case, cannot be due to hydrates.

Cadmium Chloride

Silver nitrate was used to precipitate the halogen in cadmium chloride, bromide and iodide.

Table XL—Conductivity

V	0°	12°.5	25°	35°
4	33.65	46.21	60.15	71.92
8	45.32	60.85	79.30	94.59
32	65.63	90.33	118.55	142.48
128	88.34	122.98	162.32	195.71
512	106.14	148.36	197.57	236.99
1024	113.78	159.65	212.53	258.73
2048	121.19	166.23	221.36	269.00
4096	121.03	172.78	232.06	282.43

Table XLI—Temperature Coefficients

	0°–12°.5		12°.5–25°		25°–35°	
V	Cond. units	Per cent.	Cond. units	Per cent.	Cond. units	Per cent.
4	1.00	2.97	1.12	2.42	1.18	1.96
8	1.24	2.74	1.47	2.42	1.53	1.93
32	1.97	3.01	2.26	2.50	2.39	2.02
128	2.77	3.14	3.15	2.54	3.34	2.06
512	3.38	3.18	3.94	2.66	3.94	1.99
1024	3.67	3.23	4.23	2.65	4.62	2.17
2048	3.60	2.97	4.41	2.65	4.76	2.10
4096	4.14	3.42	4.74	2.62	5.04	2.12

Table XLII—Percentage Dissociation

V	0°	12°.5	25°	35°
4	27.8	26.7	25.9	25.5
8	37.4	35.2	34.2	33.5
32	54.2	52.3	51.1	50.5
128	72.9	71.2	69.9	69.3
512	87.6	85.9	85.1	83.9
1024	93.9	92.4	91.6	91.6
2048	100.0	96.2	95.4	95.3
4096	99.9	100.0	100.0	100.0

Cadmium Bromide

Table XLIII—Conductivity

V	0°	12°.5	25°	35°
4	28.63	40.59	53.40	64.51
8	37.80	53.36	70.44	84.81
32	57.78	82.06	109.34	132.69
128	79.77	113.57	151.23	184.16
512	101.37	143.25	190.52	232.83
1024	110.69	156.85	208.48	252.81
2048	121.23	170.89	227.41	275.22
4096	123.76	174.05	232.20	280.84

Table XLIV—Temperature Coefficients

	0°–12°.5		12°.5–25°		25°–35°	
V	Cond. units	Per cent.	Cond. units	Per cent.	Cond. units	Per cent.
4	0.96	3.35	1.02	2.51	1.11	2.07
8	1.24	3.28	1.37	2.56	1.44	2.03
32	1.94	3.35	2.18	2.66	2.34	2.14
128	2.70	3.38	3.01	2.65	3.29	2.18
512	3.55	3.30	3.78	2.64	4.23	2.22
1024	3.69	3.33	4.13	2.62	4.43	2.12
2048	3.97	3.21	4.52	2.64	4.78	2.10
4096	4.02	3.25	4.65	2.67	4.86	2.79

Table XLV—Percentage Dissociation

V	0°	12°.5	25°	35°
4	23.1	23.3	23.0	23.0
8	30.5	30.6	30.3	30.2
32	46.7	47.1	47.1	47.3
128	64.4	65.2	65.1	65.6
512	81.9	82.3	82.1	82.9
1024	89.4	90.1	89.8	90.0
2048	97.9	98.2	97.9	98.0
4096	100.0	100.0	100.0	100.0

Cadmium Iodide

Table XLVI—Conductivity

V	0°	12°.5	25°	35°
4	20.45	29.76	39.84	48.41
8	24.31	35.85	48.44	59.43
32	39.45	59.23	81.53	101.22
128	62.73	93.36	127.36	157.35
512	87.06	127.74	172.93	211.90
1024	96.31	140.03	188.66	231.10
2048	109.01	157.20	209.73	256.42
4096	118.78	170.69	224.93	271.27

Table XLVII—Temperature Coefficients

	0°–12°.5		12°.5–25°		25°–35°	
V	Cond. units	Per cent.	Cond. units	Per cent.	Cond. units	Per cent.
4	0.75	3.67	0.81	2.72	0.86	2.16
8	0.92	3.78	1.01	2.82	1.10	2.27
32	1.58	4.01	1.78	3.01	1.97	2.42
128	2.45	3.90	2.72	2.91	3.00	2.36
512	3.25	3.73	3.62	2.83	3.90	2.26
1024	3.57	3.71	3.82	3.71	4.24	2.25
2048	3.86	3.54	4.20	3.67	4.67	2.23
4096	4.15	3.49	4.34	2.54	4.63	2.06

Table XLVIII—Percentage Dissociation

V	0°	12°.5	25°	35°
4	17.2	17.4	17.7	17.8
8	20.5	21.0	21.5	21.9
32	33.2	34.7	36.3	37.3
128	52.8	54.7	56.6	58.0
512	73.3	74.8	76.9	78.1
1024	81.0	82.6	83.9	85.2
2048	91.7	92.1	93.3	94.5
4096	100.0	100.0	100.0	100.0

Lead Chloride

The lead was precipitated by means of sulphuric acid and weighed as lead sulphate.

Table XLIX—Conductivity

V	0°	12°.5	25°	35°
64	104.41	144.76	188.71	224.76
128	116.27	161.56	211.43	252.17
512	133.10	186.16	246.31	293.05
1024	136.89	191.98	253.96	306.43
2048	138.88	195.16	258.49	312.13
4096	144.70	204.36	270.26	327.80

Table L—Temperature Coefficients

	0°–12°.5		12°.5–25°		25°–35°	
V	Cond. units	Per cent.	Cond. units	Per cent.	Cond. units	Per cent.
64	3.23	3.09	3.52	2.43	3.61	1.91
128	3.63	3.12	3.99	2.47	4.07	1.93
512	4.25	3.19	4.81	2.58	4.67	1.90
1024	4.41	3.22	4.96	2.58	5.25	2.07
2048	4.70	3.24	5.07	2.60	5.36	2.07
4096	4.77	3.30	5.27	2.58	5.75	2.13

Table LI—Percentage Dissociation

V	0°	12°.5	25°	35°
64	72.2	70.8	69.8	68.6
128	80.4	79.0	78.2	76.9
512	92.0	91.1	91.1	89.4
1024	94.6	93.9	94.0	93.5
2048	96.0	95.5	95.6	95.2
4096	100.0	100.0	100.0	100.0

The aluminium and chromium compounds will be taken up next for discussion. In these compounds we should expect to find strong resemblances. These are very apparent. Chromium and aluminium compounds, with respect to their conductivities, are in a class by themselves. Their very large conductivities and their exceedingly large temperature coefficients must attract attention. Their very large conductivities are due mainly to the great number of ions into which they are capable of ionizing and to hydrolysis. Judging from

their water of crystallization and from freezing point lowerings,[1] they must be hydrated to an enormous extent. Their large temperature coefficients of conductivity would also indicate this to be the fact. The change in conductivity, both with rise in temperature and with dilution, is much more gradual in the case of the aluminium salts than with those of chromium. The extremely small percentage dissociation in concentrated solutions, in the case of chromium sulphate and aluminium sulphate, is worthy of notice. This is probably connected with the fact that sulphates, especially in concentrated solution, undergo marked polymerization.

Aluminium Chloride

The aluminium was determined by precipitating the hydroxide and weighing as the oxide Al_2O_3. This was done also in the case of aluminium nitrate and aluminium sulphate.

Table LII—Conductivity

V	0°	12°.5	25°	35°
4	105.90	147.40	193.51	232.54
8	120.22	168.23	220.86	266.58
32	142.21	200.06	265.12	322.18
128	162.66	231.08	308.80	377.28
512	176.77	252.75	341.24	421.06
1024	184.58	266.73	360.56	446.95
2048	193.37	279.49	381.44	472.46
4096	199.03	290.06	398.79	499.92

Table LIII—Temperature Coefficients

	0°–12°.5		12°.5–25°		25°–35°	
V	Cond. units	Per cent.	Cond. units	Per cent.	Cond. units	Per cent.
4	3.32	3.14	3.69	2.50	3.90	2.02
8	3.84	3.19	4.21	2.50	4.57	2.07
32	4.63	3.26	5.21	2.60	5.71	2.15
128	5.47	3.36	6.22	2.69	6.85	2.22
512	6.08	3.07	7.08	2.80	7.98	2.34
1024	6.57	3.55	7.51	2.82	8.64	2.40
2048	6.89	3.56	8.16	2.92	9.10	2.39
4096	7.28	3.66	8.70	3.00	10.11	2.54

[1] Jones and Getman: THIS JOURNAL, **31**, 303 (1904). Publication No. **60**, Carnegie Institution of Washington.

Table LIV—Percentage Dissociation

V	0°	12°.5	25°	35°
4	53.2	50.8	48.5	46.5
8	60.4	58.0	55.4	53.3
32	71.5	69.0	66.5	64.4
128	81.7	79.7	77.4	75.5
512	88.8	87.1	85.5	84.2
1024	92.8	91.9	90.4	89.4
2048	97.2	96.3	95.6	94.5
4096	100.0	100.0	100.0	100.0

Aluminium Nitrate

Table LV—Conductivity

V	0°	12°.5	25°	35°
4	102.82	139.22	180.52	216.54
8	115.67	158.84	206.89	248.82
32	136.32	188.54	247.70	299.96
128	156.18	217.14	287.05	349.49
512	166.97	234.81	313.05	384.43
1024	173.45	247.08	332.20	410.18
2048	179.32	255.68	345.82	428.32
4096	187.89	272.12	372.07	462.84

Table LVI—Temperature Coefficients

	0°–12°.5		12°.5–25°		25°–35°	
V	Cond. units	Per cent.	Cond. units	Per cent.	Cond. units	Per cent.
4	2.91	2.83	3.30	2.37	3.60	1.99
8	3.45	2.98	3.84	2.42	4.19	2.03
32	4.18	3.07	4.75	2.51	5.23	2.11
128	4.88	3.12	5.60	2.58	6.25	2.18
512	5.45	3.25	6.28	2.67	7.17	2.28
1024	5.93	3.40	6.86	2.77	7.86	2.36
2048	6.19	3.44	7.31	2.83	8.37	2.39
4096	6.90	4.53	8.19	2.95	9.32	2.45

Table LVII—Percentage Dissociation

V	0°	12°.5	25°	35°
4	54.7	51.2	48.5	46.8
8	61.6	58.4	55.6	53.8
32	72.5	69.3	66.6	64.9
128	83.1	79.8	77.1	75.6
512	88.9	86.3	84.1	83.1
1024	92.3	90.8	89.3	88.7
2048	95.4	94.0	92.9	92.6
4096	100.0	100.0	100.0	100.0

Aluminium Sulphate

Table LVIII—Conductivity

V	0°	12°.5	25°	35°
4	51.90	71.81	92.40	107.72
8	65.21	89.81	114.44	132.46
32	89.50	123.63	158.01	183.51
128	121.87	169.38	219.04	266.22
512	164.08	230.86	301.01	358.79
1024	191.95	271.31	359.16	433.51
2048	222.31	317.20	425.03	518.19
4096	262.35	378.23	514.06	634.78

Table LIX—Temperature Coefficients

	0°–12°.5		12°.5–25°		25°–35°	
V	Cond. units	Per cent.	Cond. units	Per cent.	Cond. units	Per cent.
4	1.59	3.06	1.65	2.30	1.53	1.66
8	1.97	3.02	1.97	2.19	1.80	1.57
32	2.73	3.05	2.75	2.23	2.55	1.61
128	3.80	3.12	3.97	2.34	4.72	2.16
512	5.34	3.25	5.61	2.43	5.78	1.79
1024	6.34	3.30	7.03	2.59	7.44	2.07
2048	7.59	3.41	8.63	2.72	9.32	2.19
4096	9.27	3.53	10.87	2.87	12.07	2.35

Table LX—Percentage Dissociation

V	0°	12°.5	25°	35°
4	19.8	19.0	18.0	17.0
8	24.9	23.7	22.3	20.9
32	34.1	32.7	30.7	28.9
128	46.5	44.8	42.6	41.9
512	62.5	61.0	58.5	56.5
1024	73.2	71.7	69.9	68.3
2048	84.7	83.9	82.7	81.6
4096	100.0	100.0	100.0	100.0

Chromium Chloride

The chromium was weighed as the oxide Cr_2O_3 in the case of both chromium chloride and chromium sulphate.

Table LXI—Conductivity

V	0°	12°.5	25°	35°
4	86.30	116.97	153.32	199.10
8	104.53	138.83	184.18	243.55
32	130.03	182.75	245.00	319.15
128	162.34	231.28	313.45	393.62
512	188.46	272.50	372.34	465.10
1024	200.21	294.55	403.58	504.31
2048	214.48	316.60	434.36	543.02
4096	229.73	341.14	467.61	580.16

Table LXII—Temperature Coefficients

	0°–12°.5		12°.5–25°		25°–35°	
V	Cond. units	Per cent.	Cond. units	Per cent.	Cond. units.	Per cent.
4	2.45	2.84	2.91	2.49	4.58	2.99
8	2.74	2.62	3.63	2.62	5.94	3.23
32	4.22	3.25	4.98	2.73	7.42	3.03
128	5.52	3.40	6.57	2.84	8.02	2.55
512	6.72	3.57	7.99	2.93	9.28	3.95
1024	7.54	3.77	8.72	2.96	10.07	2.50
2048	8.18	3.82	9.42	2.98	10.87	2.50
4096	8.91	3.88	10.12	2.97	11.26	2.41

Table LXIII—Percentage Dissociation

V	0°	12°.5	25°	35°
4	37.6	34.3	32.8	34.3
8	45.5	40.7	39.4	42.0
32	56.6	53.6	52.4	55.0
128	70.7	67.8	67.0	67.9
512	82.1	79.9	79.6	80.2
1024	87.2	86.4	86.3	86.9
2048	93.3	92.9	92.9	93.6
4096	100.0	100.0	100.0	100.0

Chromium Sulphate

Table LXIV—Conductivity

V	0°	12°.5	25°	35°
4	58.14	78.48	99.64	116.41
8	77.85	103.64	130.18	151.17
32	120.59	158.67	197.34	230.37
128	169.08	225.60	283.56	338.67
512	215.36	292.66	376.23	472.16
1024	240.48	329.96	459.83	561.76
2048	293.38	405.65	534.55	708.14
4096	315.39	445.16	598.46	808.29

Table LXV—Temperature Coefficients

	0°–12°.5		12°.5–25°		25°–35°	
V	Cond. units	Per cent.	Cond. units	Per cent.	Cond. units	Per cent.
4	1.63	2.80	1.69	2.15	1.68	1.69
8	2.06	2.65	2.12	2.05	2.10	1.61
32	3.05	2.54	2.46	1.55	3.30	1.67
128	4.52	2.67	4.64	2.06	5.51	1.94
512	6.18	2.87	4.69	1.60	9.59	2.55
1024	7.16	2.98	10.39	3.15	10.10	2.22
2048	8.98	3.06	10.31	2.54	17.36	3.25
4096	10.38	3.29	12.26	2.75	20.98	3.51

Table LXVI—Percentage Dissociation

V	0°	12°.5	25°	35°
4	18.4	17.6	16.6	14.4
8	24.7	23.3	21.7	18.7
32	38.2	35.6	33.0	28.5
128	53.6	50.7	47.4	41.9
512	68.3	65.7	62.8	58.5
1024	76.2	74.1	76.8	69.5
2048	93.0	91.1	89.3	87.7
4096	100.0	100.0	100.0	100.0

In the next group will be considered manganous sulphate, silver nitrate, copper sulphate and cobalt bromide. Manganous sulphate calls for no comment. The data obtained for silver nitrate are remarkably similar to those obtained for ammonium nitrate. It apparently behaves as any other ordinary, unhydrated, binary compound. It differs from ammonium nitrate in that its percentage dissociation, apparently decreasing with rise in temperature from 0° to 25°, increases somewhat at 35°.

The data for copper sulphate resemble strikingly those obtained for manganous sulphate, cadmium bromide and cadmium iodide. At ordinary temperatures manganous sulphate and copper sulphate have the same amount of water of crystallization. That their temperature coefficients should be approximately the same is not surprising; but that the temperature coefficients of cadmium chloride and cadmium bromide, crystallizing with less water, and cadmium iodide, crystallizing with no water, should be the same is surprising.

The temperature coefficients of conductivity of cobalt bromide indicate much hydration, as would be expected from its water of crystallization.

Manganous Sulphate

The manganese was weighed as the pyrophosphate.

Table LXVII—Conductivity

V	0°	12°.5	25°	35°
4	37.25	51.80	67.17	79.11
8	44.11	61.37	79.77	94.06
32	59.65	83.47	109.27	129.72
128	79.46	111.74	147.24	176.10
512	97.99	138.76	184.58	222.69
1024	107.12	152.31	202.94	245.72
2048	116.15	165.28	221.33	268.33
4096	124.47	177.56	238.20	289.39

Table LXVIII—Temperature Coefficients

	0°–12°.5		12°.5–25°		25°–35°	
V	Cond. units	Per cent.	Cond. units	Per cent.	Cond. units	Per cent.
4	1.16	3.11	1.23	2.38	1.19	1.77
8	1.38	3.13	1.47	2.40	1.43	1.79
32	1.91	3.20	2.06	2.47	2.05	1.88
128	2.58	3.25	2.84	2.54	2.89	1.96
512	3.26	3.33	3.67	2.64	3.81	2.06
1024	3.62	3.38	4.05	2.66	4.28	2.11
2048	3.93	3.38	4.48	2.71	4.70	2.12
4096	4.25	3.42	4.85	2.73	5.12	2.15

Table LXIX—Percentage Dissociation

V	0°	12°.5	25°	35°
4	29.9	29.2	28.2	27.3
8	35.4	34.6	33.5	32.5
32	47.9	47.0	45.9	44.8
128	63.8	62.9	61.8	60.8
512	78.7	78.1	77.5	76.9
1024	86.1	85.8	85.2	84.9
2048	93.3	93.1	92.9	92.7
4096	100.0	100.0	100.0	100.0

Silver Nitrate

The silver was weighed as the chloride.

Table LXX—Conductivity

V	0°	12°.5	25°	35°
4	51.43	70.55	91.63	109.95
8	56.01	76.68	99.80	120.37
32	61.80	85.30	111.20	133.14
128	65.79	91.06	119.14	142.67
512	69.24	94.99	125.23	148.77
2048	69.83	96.67	126.81	151.24
4096	71.03	99.03	129.68	153.32

Table LXXI—Temperature Coefficients

	0°–12°.5		12°.5–25°		25°–35°	
V	Cond. units	Per cent.	Cond. units	Per cent.	Cond. units	Per cent.
4	1.53	2.98	1.69	2.40	1.83	2.00
8	1.65	2.95	1.65	2.15	2.06	2.06
32	1.88	2.94	2.07	2.43	2.19	1.97
128	2.02	2.94	2.25	2.47	2.35	1.97
512	2.06	2.98	2.42	2.55	2.35	1.87
2048	2.15	3.01	2.41	2.49	2.44	1.92
4096	2.24	3.15	2.45	2.47	2.36	1.82

Table LXXII—Percentage Dissociation

V	0°	12°.5	25°	35°
4	72.4	71.3	70.6	71.7
8	78.8	77.4	76.9	78.5
32	87.0	86.2	85.7	86.8
128	92.6	92.0	91.8	93.1
512	97.4	95.9	96.5	97.0
2048	98.3	97.6	97.7	98.7
4096	100.0	100.0	100.0	100.0

Cobalt Bromide

This salt was precipitated by means of silver nitrate, and the bromine determined from the weight of silver bromide obtained.

Table LXXIII—Conductivity

V	0°	12°.5	25°	35°
4	87.82	120.24	155.60	196.30
8	95.04	131.29	171.30	204.48
32	105.56	147.10	193.09	233.04
128	115.88	162.19	214.02	259.91
512	119.47	169.42	224.49	273.44
1024	120.80	173.38	231.56	281.16
2048	124.00	174.68	234.28	282.65
4096	125.45	177.93	236.78	289.34

Table LXXIV—Temperature Coefficients

	0°–12°.5		12°.5–25°		25°–35°	
V	Cond. units	Per cent.	Cond. units	Per cent.	Cond. units	Per cent.
4	2.59	2.95	2.83	2.35	4.07	2.62
8	2.90	3.05	3.20	2.44	3.32	1.94
32	3.32	3.15	3.68	2.50	4.00	2.07
128	3.71	3.20	4.15	2.56	4.59	2.15
512	4.00	3.35	4.41	2.60	4.90	2.18
1024	4.21	3.49	4.65	2.68	4.96	2.14
2048	4.05	3.27	4.77	2.73	4.84	2.07
4096	4.20	3.35	4.71	2.65	5.26	2.22

Table LXXV—Percentage Dissociation

V	0°	12°.5	25°	35°
4	70.0	67.6	65.7	67.8
8	75.7	73.8	72.3	70.7
32	84.1	82.7	81.5	80.5
128	92.3	92.0	90.4	89.8
512	95.2	95.2	94.8	94.5
1024	96.3	97.5	97.8	97.2
2048	98.8	98.2	98.9	97.7
4096	100.0	100.0	100.0	100.0

Copper Sulphate

The sulphuric acid in this salt was precipitated and weighed as barium sulphate.

Table LXXVI—Conductivity

V	0°	12°.5	25°	35°
2	30.06	42.12	55.11	65.15
8	42.30	59.35	77.33	91.16
32	57.24	80.53	105.64	124.94
128	76.91	108.74	143.21	170.60
512	97.88	138.92	184.97	221.08
1024	105.85	150.86	202.57	245.05
2048	113.36	161.78	217.71	264.44
4096	119.18	171.07	231.27	281.42

Table LXXVII—Temperature Coefficients

	0°–12°.5		12°.5–25°		25°–35°	
V	Cond. units	Per cent.	Cond. units	Per cent.	Cond. units	Per cent.
2	0.96	3.19	1.04	2.47	1.00	1.82
8	1.36	3.22	1.44	2.43	1.38	1.79
32	1.86	3.25	2.01	2.50	1.93	1.83
128	2.54	3.30	2.76	2.54	2.74	1.91
512	3.28	3.35	3.68	2.65	3.61	1.95
1024	3.60	3.40	4.14	2.74	4.25	2.10
2048	3.87	3.41	4.47	2.76	4.67	2.15
4096	4.15	3.48	4.82	2.82	5.02	2.17

Table LXXVIII—Percentage Dissociation

V	0°	12°.5	25°	35°
2	25.2	24.6	23.8	23.2
8	35.5	34.7	33.4	32.4
32	48.0	47.1	45.7	44.4
128	64.5	63.6	61.9	60.6
512	82.1	81.2	80.0	78.6
1024	88.8	88.2	87.6	87.1
2048	95.1	94.6	94.1	94.0
4096	100.0	100.0	100.0	100.0

The conductivity values obtained for uranyl sulphate and uranyl acetate do not agree satisfactorily with those obtained by West.[1] His solutions were evidently standardized on a different basis. It should be noticed that the temperature coefficients, in conductivity units, of uranyl sulphate decrease with rise in temperature through $V = 512$. After this dilution they increase, as in the case of the other uranyl salts. The percentage dissociation of uranyl acetate apparently

[1] THIS JOURNAL, **44**, 537 (1910).

increases with rise in temperature through $V = 128$. The more dilute solutions show a decrease with rise in temperature. This may be seen in the curve for uranyl acetate which follows.

Uranyl Chloride

The uranium in uranyl chloride, nitrate, sulphate and acetate was precipitated by means of ammonium hydroxide and weighed as the oxide U_3O_8.

Table LXXIX—Conductivity

V	0°	12°.5	25°	35°
4	101.45	139.09	180.45	214.70
8	110.48	157.64	206.01	246.51
32	133.05	186.56	246.12	297.84
128	148.39	209.75	279.00	339.40
512	155.98	220.70	296.56	360.44
1024	161.02	231.37	311.92	383.88
2048	168.42	242.69	328.24	405.98
4096	174.98	254.22	348.16	433.68

Table LXXX—Temperature Coefficients

	0°–12°.5		12°.5–25°		25°–35°	
V	Cond. units	Per cent.	Cond. units	Per cent.	Cond. units	Per cent.
4	3.01	2.97	3.31	2.38	3.43	1.90
8	3.77	3.41	3.87	2.46	4.05	1.97
32	4.28	3.22	4.76	2.55	5.17	2.10
128	4.91	3.31	5.54	2.64	6.04	2.17
512	5.18	3.32	6.07	2.75	6.39	2.16
1024	5.63	3.50	6.44	2.78	7.20	2.31
2048	5.94	3.53	6.84	2.82	7.77	2.37
4096	6.34	3.62	7.52	2.96	8.55	2.46

Table LXXXI—Percentage Dissociation

V	0°	12°.5	25°	35°
4	58.0	54.7	51.8	49.5
8	63.1	62.0	59.2	56.8
32	76.0	73.4	70.7	68.7
128	84.8	82.5	80.2	78.2
512	89.1	86.8	85.2	83.1
1024	92.0	91.0	89.6	88.5
2048	96.3	95.5	94.3	93.6
4096	100.0	100.0	100.0	100.0

Uranyl Nitrate

Table LXXXII—Conductivity

V	0°	12°.5	25°	35°
4	74.91	102.01	132.91	158.84
8	83.44	114.71	150.57	181.20
32	97.22	136.35	180.64	219.38
128	110.14	153.84	207.89	254.21
512	116.33	166.65	224.95	277.35
1024	123.14	177.76	241.47	298.63
2048	128.92	187.20	255.38	317.44
4096	136.77	200.10	274.50	343.09

Table LXXXIII—Temperature Coefficients

	0°–12°.5		12°.5–25°		25°–35°	
V	Cond. units	Per cent.	Cond. units	Per cent.	Cond. units	Per cent.
4	2.17	2.90	2.47	2.42	2.59	1.95
8	2.50	3.00	3.07	2.68	3.06	2.03
32	3.13	3.22	3.54	2.60	3.87	2.14
128	3.66	3.32	4.16	2.67	4.63	2.23
512	4.03	3.47	4.66	2.80	5.24	2.33
1024	4.37	3.55	5.10	2.87	5.72	2.37
2048	4.66	3.62	5.46	2.92	6.21	2.43
4096	5.07	3.71	5.95	2.97	6.86	2.50

Table LXXXIV—Percentage Dissociation

V	0°	12°.5	25°	35°
4	54.8	51.0	48.4	46.3
8	61.0	57.3	54.9	52.8
32	71.1	68.1	65.8	63.9
128	80.5	77.9	75.8	74.1
512	85.0	83.3	82.0	80.8
1024	90.0	88.8	88.0	87.1
2048	94.2	93.6	93.1	92.5
4096	100.0	100.0	100.0	100.0

Uranyl Sulphate

Table LXXXV—Conductivity

V	0°	12°.5	25°	35°
8	78.13	99.77	120.82	136.43
32	100.65	129.52	156.80	176.52
128	128.62	166.72	203.02	229.42
512	157.54	207.90	257.69	295.20
1024	175.68	235.28	296.95	343.01
2048	191.68	260.77	332.57	391.00
4096	203.33	285.05	373.65	446.33

Table LXXXVI—Temperature Coefficients

	0°–12°.5		12°.5–25°		25°–35°	
V	Cond. units	Per cent.	Cond. units	Per cent.	Cond. units	Per cent.
8	1.73	2.22	1.68	1.68	1.56	1.29
32	2.31	2.30	2.18	1.68	1.97	1.26
128	3.05	2.37	2.90	1.74	2.64	1.30
512	4.03	2.56	3.98	1.91	3.75	1.46
1024	4.77	2.72	4.93	2.10	4.61	1.55
2048	5.53	2.89	5.74	2.20	5.84	1.76
4096	6.54	3.22	7.09	2.49	7.27	1.95

Table LXXXVII—Percentage Dissociation

V	0°	12°.5	25°	35°
8	38.4	35.0	32.3	30.6
32	49.5	45.4	42.0	39.6
128	63.2	58.5	54.3	51.4
512	77.5	72.9	69.0	66.2
1024	86.4	82.5	79.5	76.9
2048	94.2	91.5	89.0	87.6
4096	100.0	100.0	100.0	100.0

Uranyl Acetate

Table LXXXVIII—Conductivity

V	0°	12°.5	25°	35°
8	30.59	42.75	56.53	68.12
32	39.65	55.08	72.25	86.67
128	51.48	70.66	91.34	108.52
512	63.57	86.06	110.47	129.06
1024	70.13	94.74	120.37	141.12
2048	76.81	103.65	131.78	154.46
4096	83.75	113.81	145.10	170.54

Table LXXXIX—Temperature Coefficients

	0°–12°.5		12°.5–25°		25°–35°	
V	Cond. units	Per cent.	Cond. units	Per cent.	Cond. units	Per cent.
8	0.97	3.12	1.10	2.57	1.16	2.05
32	1.23	3.10	1.37	2.49	1.44	1.99
128	1.53	2.97	1.65	2.34	1.72	1.88
512	1.80	2.83	1.95	2.26	1.86	1.68
1024	1.97	2.81	2.05	2.16	2.08	1.73
2048	2.15	2.80	2.25	2.17	2.27	1.72
4096	2.41	2.88	2.50	2.20	2.54	1.75

Table XC—Percentage Dissociation

V	0°	12°.5	25°	35°
8	36.5	37.6	39.0	40.0
32	47.3	48.4	48.8	50.8
128	61.5	62.1	63.0	63.7
512	75.9	75.6	76.1	75.7
1024	83.7	83.3	83.0	82.8
2048	91.7	91.1	90.8	90.6
4096	100.0	100.0	100.0	100.0

PLATES

So far little or nothing has been said in regard to the percentage dissociation of the salts studied. Attention will be called to these by means of curves. The curves of ten of the thirty salts showed the percentage dissociation to be almost a linear function of rise in temperature. Plotting percentage dissociation as ordinates against rise in temperature as abscissae, for each dilution, in ten cases out of the thirty, curves were obtained resembling the one for aluminium sulphate, Fig. I. The other 20 salts all showed variations in the maxima or minima. Some of these are very slight. Diagrams of the most striking variations follow. The salts giving curves showing the percentage dissociation to be a linear function of rise in temperature were acid ammonium sulphate, aluminium nitrate, aluminium chloride, aluminium sulphate, uranyl chloride, uranyl sulphate, uranyl nitrate, chromium sulphate, cadmium chloride and manganous sulphate. The others showed more or less variations, the most striking being here represented.

Fig. II is very interesting, showing in the case of cadmium iodide the increase in percentage dissociation with rise of temperature from $V = 8$ to $V = 2048$.

From the curve, Fig. III, it is easily seen that the percentage dissociation of chromium chloride increases decidedly with rise in temperature between 25° and 35°. The increase becomes less and less as the dilution increases.

Uranyl acetate shows an increase in percentage dissociation in the more concentrated solutions, but at greater dilutions gives a falling curve (Fig. IV).

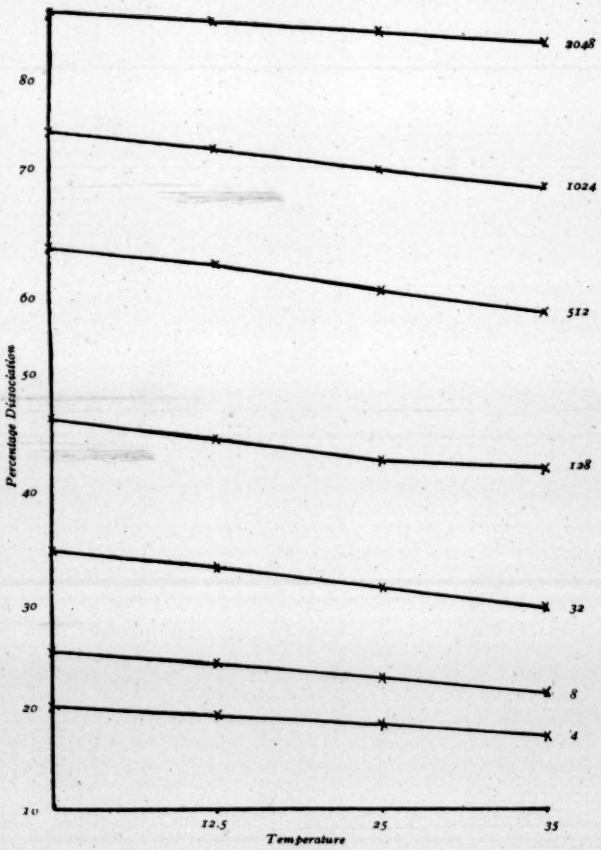

Fig. I—Aluminium Sulphate

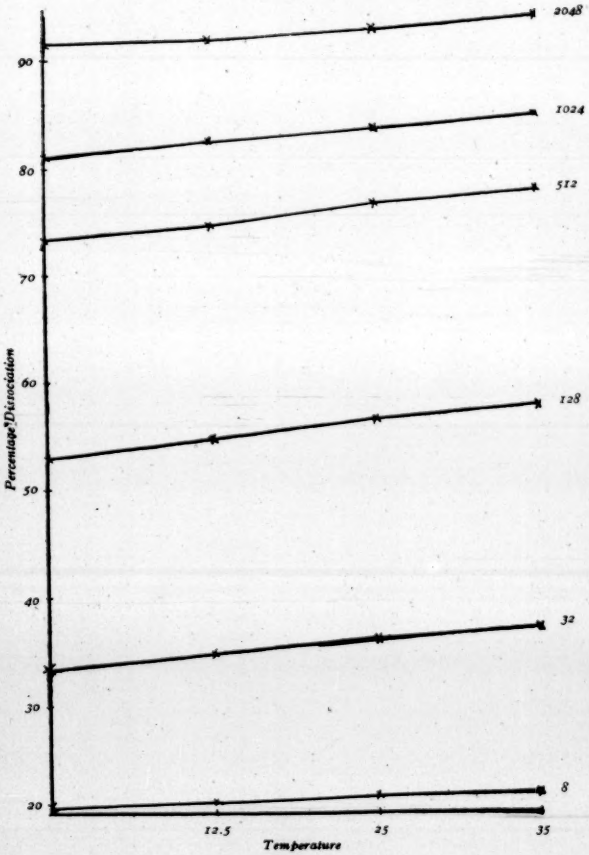

Fig. II—Cadmium Iodide

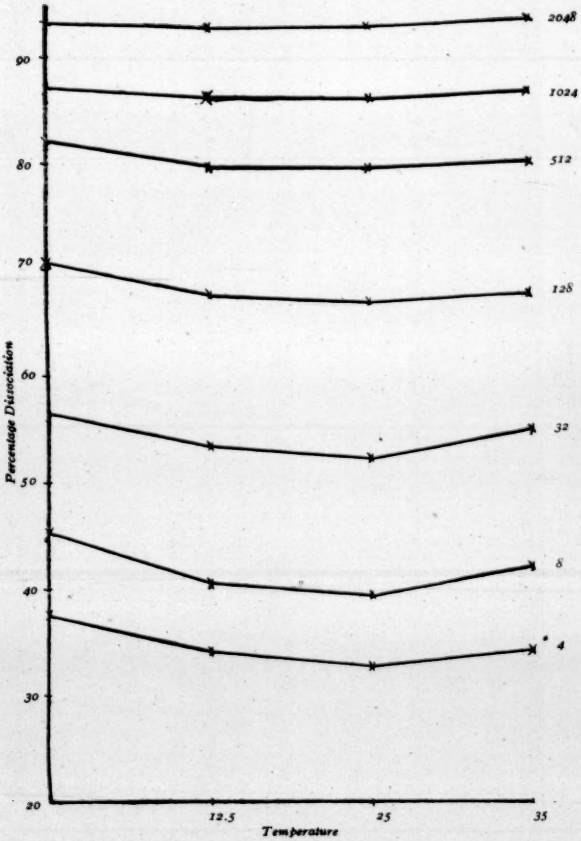

Fig. III—Chromium Chloride

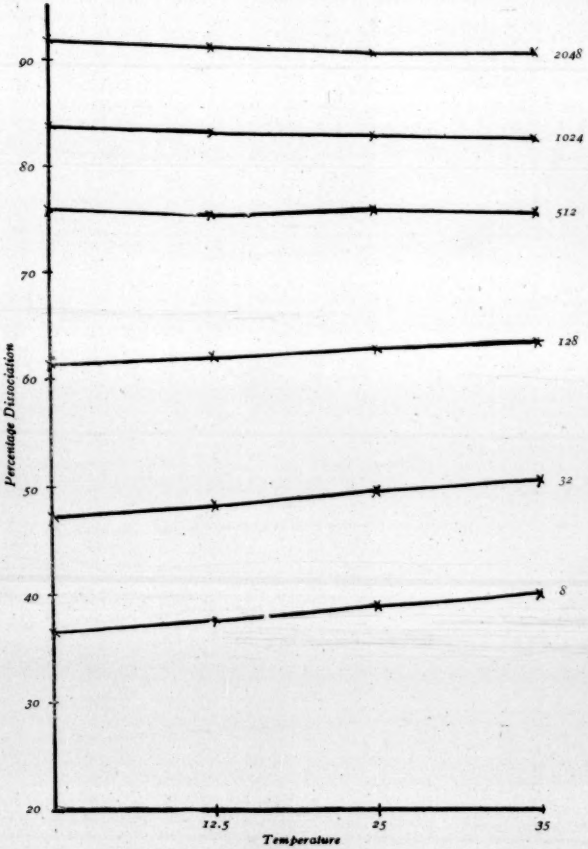

Fig. IV—Uranyl Acetate

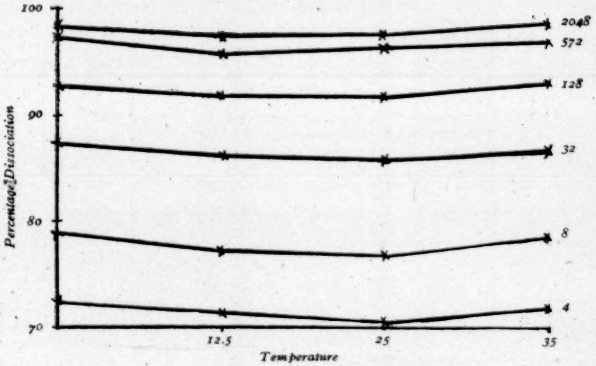

Fig. V—Silver Nitrate

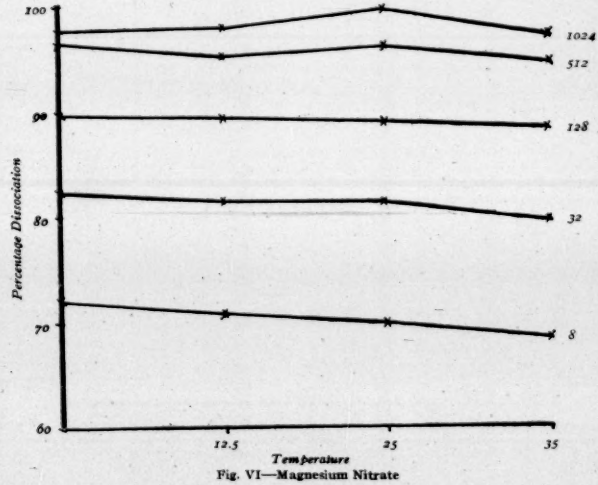

Fig. VI—Magnesium Nitrate

Silver nitrate shows a decided increase in percentage dissociation with rise in temperature from $V = 4$ to $V = 2048$. See Fig. V.

The curves representing magnesium nitrate and magnesium bromide (Figs. VI and VII) show a remarkable resemblance. The maxima at higher dilutions are pronounced.

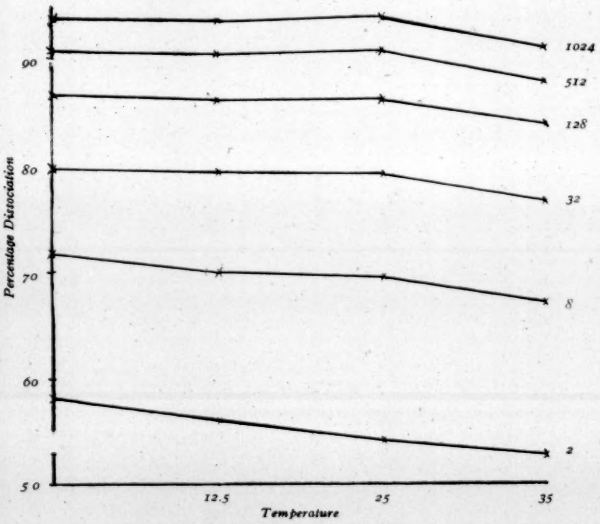

Fig. VII—Magnesium Bromide

An examination of the curves raised the question, what produces this variation? The apparent increase in percentage dissociation with rise in temperature would, naturally, be thought to be due to hydration. When there is little or no hydration the question becomes more difficult to answer. If, however, the ions are assumed to be complex, rise in temperature would bring about greater dissociation, and the effect

would be just the same as if hydrates had been present. It is difficult to differentiate the two factors. That hydrates exist is not doubted. The complexity of the ions is not so well established, so that we shall present arguments only for the latter. If the change were a gradual increase, it might be attributed easily to hydration, but a change from an increase to a decrease in dissociation could not be accounted for in this way; whereas complex ions once dissociated might reach a state where recombination would take place. Moreover, the amount of hydration has been found to depend on the amount of water of crystallization. In several of the preceding salts, notably in the case of cadmium compounds, cadmium iodide, which has no water of crystallization, is found to have temperature coefficients of conductivity equal in magnitude to those of cadmium chloride, cadmium bromide and copper sulphate, all of which have water of crystallization. Lead chloride, also, which has no water of crystallization, has temperature coefficients which compare well with those of substances that are much hydrated, i. e., copper sulphate and cobalt bromide. This would indicate that there must be some other factor present producing the same effect as hydration.

SUMMARY

1. In the main the results obtained in the case of the thirty salts studied tend to confirm the earlier results.

2. Without exception conductivity increases with rise in temperature and with dilution.

3. The temperature coefficients of conductivity expressed in conductivity units, with two exceptions, increase with rise in temperature, while the temperature coefficients expressed in percentage decrease.

4. Salts greatly hydrated have large temperature coefficients. The amount of hydration, judged by the temperature coefficients, seems closely related to the water of crystallization.

5. The apparent exceptions to the results earlier obtained, viz., an increase in percentage dissociation with rise in temperature and a large temperature coefficient when there is no

reason to expect large hydration, point, in the opinion of the authors, strongly to the view advanced above, that inductive action takes place through the solvent between charged ions and neutral molecules, and that this gives rise to complex molecules and ions in solution.

After sufficient work has been done in this field, it is hoped to bring together all of the conductivity and dissociation data obtained in this laboratory and to publish them as a monograph. However, before this is done it is intended to repeat the work with every substance, where the repetition is not already complete, starting with new material, repurifying, restandardizing and remeasuring the conductivity.

Work will be continued in this laboratory along the lines indicated above, probably for at least the next ten years, and there will be five investigators working here in this field during the next academic year.

JOHNS HOPKINS UNIVERSITY
May, 1911

REVIEWS

UEBER KATALYSE. VON WILHELM OSTWALD. Rede gehalten am 12 December, 1909, bei Empfang des Nobelpreises für Chemie. Zweite Auflage. Leipzig: Akademische Verlagsgesellschaft m. b. H. 1911. Price, M. 1.50.

It is not surprising that a second edition of this interesting lecture has been called for. The circumstances, the subject, the lecturer form a strong combination. Every chemist will find it profitable to read the lecture, and not the least interesting part is that which deals with the author himself. He does not apologize for withdrawing from his activity in experimental work but offers an explanation. Lothar Meyer had warned him against too close application and possible physical exhaustion, but Ostwald took the ground that it is much more important to keep at the work, even to the point of complete exhaustion, than to spare the individual in the hope that he may be able to contribute more by living longer.

The author's references to Berzelius and his discussion of catalysis show once more what is well known to those who have carefully studied the history of any branch of science,

that the great original is often held responsible for ideas which he never entertained.

The phenomena of catalysis are among the most interesting and important of all chemical phenomena, and while this lecture furnishes anything but a systematic treatise on the subject its reading will no doubt increase the interest of the reader. I. R.

OSNOVI PHYSICHESKOI CHEMIE (The Elements of Physical Chemistry). BY PROF. HARRY C. JONES. Translated by PROF. E. V. BIRON, I. I. ZHUKOFF and A. V. SOPOZHNIKOFF. St. Petersburg: A. S. Suvorin. 1911. Price, 5 Rub. 75 kop.

The importance of Russian as a medium of scientific communications is now well established, and chemistry in particular is represented in that language by an extensive literature of original work and translations. The above translation of the fourth English edition of a well-known and popular work appears to be careful and well written. The printing and illustrations are clear and the paper is good. B. B. T.

ALCOHOLIC FERMENTATION. BY ARTHUR HARDEN, PH.D., D.SC., F.R.S., Head of the Biochemical Department, Lister Institute, Chelsea. Monographs on Biochemistry, edited by R. H. ADERS PLIMMER and F. G. HOPKINS. London, New York, Bombay and Calcutta: Longmans, Green & Co. 1911. pp. ix + 128. Price, $1.25.

It is not too much to say that the subject of alcoholic fermentation is one of the most interesting and important in the whole field of biochemistry, and since the discovery of zymase by Buchner in 1896, our knowledge of the process has made rapid progress. In the historical introduction the author reviews the gradual development of our knowledge of alcoholic fermentation in a most interesting and stimulating manner. This is followed by a chapter on zymase and its properties, in which the masterly researches of Buchner and others are brought to the attention of the reader. Other valuable and suggestive chapters in the monograph are those on thefunction of phosphates in alcoholic fermentation, the co-enzyme of yeast juice, and the by-products of alcoholic fermentation. The value of the monograph is further enhanced by a comprehensive bibliography containing two hundred and seventy-two (272) references to the extensive literature of this subject. In the opinion of the writer, the value of this monograph lies not only in the fact that it brings before the reader an accurate and comprehensive picture of our present knowledge of alcoholic fermentation, but also in that it will stimulate further investigation in this promising field of biochemical research.

JOSEPH H. KASTLE.

THE FATS. By J. B. LEATHES, M.A., M.B., F.R.C.S., Professor of Pathological Chemistry in the University of Toronto. Monographs on Biochemistry, edited by R. H. ADERS PLIMMER and F. G. HOPKINS. London, New York, Bombay and Calcutta: Longmans, Green & Company. 1910. pp. ix + 138.

According to the author the object of this monograph is twofold: first, to acquaint the physiologist with the recent advances in the chemistry of fats; and, second, to enable the chemist, familiar with the chemistry of fats, to look at the subject from a standpoint of the biologist. In its present shape the book is such as to indicate that the author has abundantly attained his end. The first three chapters are devoted to a brief description of the fats and fatty acids, to the extraction and methods of estimating fats in animal tissues, to the physical properties of fats, and the methods employed in their separation and identification. While not easy reading, these three chapters contain a wealth of physical and chemical data which one would scarcely expect to find in a volume of only 138 pages, and which will prove immensely valuable and convenient to those interested in this line of work. The last chapter of the monograph, entitled "The Physiology of Fats," is intensely interesting and is written in admirable style. Section C of this chapter, especially, gives us much to think about, and the subjects therein considered are such as to raise the fats to a level of biological significance hitherto attained only by the proteins. Hitherto we have been accustomed to look upon the fats solely as convenient and efficient forms of reserve material. When we recall, however, that 50 milligrams of cerebronic acid, which contains no nitrogen, will neutralize from six to nine hundred lethal doses of tetanus toxin, we begin to look at the fats in an altogether new and significant light.

JOSEPH H. KASTLE.

AN INTRODUCTION TO BACTERIOLOGICAL AND ENZYME CHEMISTRY. By GILBERT J. FOWLER, D.Sc., F.I.C., Lecturer in Bacteriological Chemistry in the Public Health Department, Victoria University of Manchester, Examiner in Biological Chemistry to the Institute of Chemistry of Great Britain and Ireland. New York: Longmans, Green & Co. London: Edward Arnold. pp. vi + 328. Price, $2.10.

The processes ordinarily included under the head of bacteriological and enzyme chemistry are assuming a continually increasing importance in their economic and scientific aspects, and advances in this field of work rapidly make their way into our domestic, civic and industrial life. From the time of Pasteur's epoch-making researches upon beer, wine and vinegar, the importance of the part played by the organized and un-

organized ferments has come more and more to be recognized and utilized in the arts and manufactures. As the author points out, however, in his preface, we have no elementary book serving as a reasonably comprehensive and accurate guide to the vast literature of this subject. In the writing of this very readable book the author has conferred a boon upon English-speaking students seeking a knowledge of the chemistry of bacteriological and zymotic processes; and, in my opinion, the chemist, the bacteriologist, the student of agriculture, and the sanitary engineer will all find in it something of interest and of value.

JOSEPH H. KASTLE.

DIE SCHWELTEERE, IHRE GEWINNUNG UND VERARBEITUNG. Von DR. W. SCHEITHAUER, Direktor. Mit 70 Figuren im Text. (Chemische Technologie in Einzeldarstellungen, herausgegeben von FERDINAND FISCHER.) Leipzig: Verlag von Otto Spamer. 1911. S. viii + 192. Preis geheftet, M. 8.75; gebunden, M. 10.

This deals very fully with the distil ation of brown coal and bituminous shales, more particularly in Thuringia, Messel and Scotland. Not only is the apparatus described but also the method of working yields and treatment of by-products. A chapter follows upon candle-making from the wax produced and two chapters upon the chemical composition of the distillates and the laboratory tests. The book opens with a short historical sketch and closes with some statistics.

The volume is one of Fischer's noted Technological Series and may be cordially recommended to all interested.

A. H. GILL.